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Assessment of the Effects of Chlorinated Seawater from Power Plants on Aquatic Organisms

TRW, Inc, Redondo Beach, CA

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16. ABSTRACT The report gives a detailed review of past and present research efforts on the effects of chlorinated seawater from power plants on aquatic organisms. It includes: (1) a characterization of chemical species contained in power plant seawater discharges; (2) a review of the amperometric titration method for residual chlorine determinations in seawater; and (3) an analysis of the toxicity of compounds formed by chlorination of seawater. The review concluded that (1) the toxicity of chlorinated seawater effluent is due primarily to various oxidant residuals produced by chlorination, rather than to residual chlorine itself; (2) the amperometric titration method is adequate to determine safe oxidant levels when identification of specific compounds is not required; (3) bromoform is a principal contributor to toxicity in power plant discharges (because of volatility and degradability, bromoform is not expected to be as toxic as chloroform); and (4) other compounds suspected of causing toxicity have not been clearly identified. Further studies into the actual components present in chlorinated power plant seawater discharges are necessary to determine exactly which compounds are responsible for the toxicological effects.

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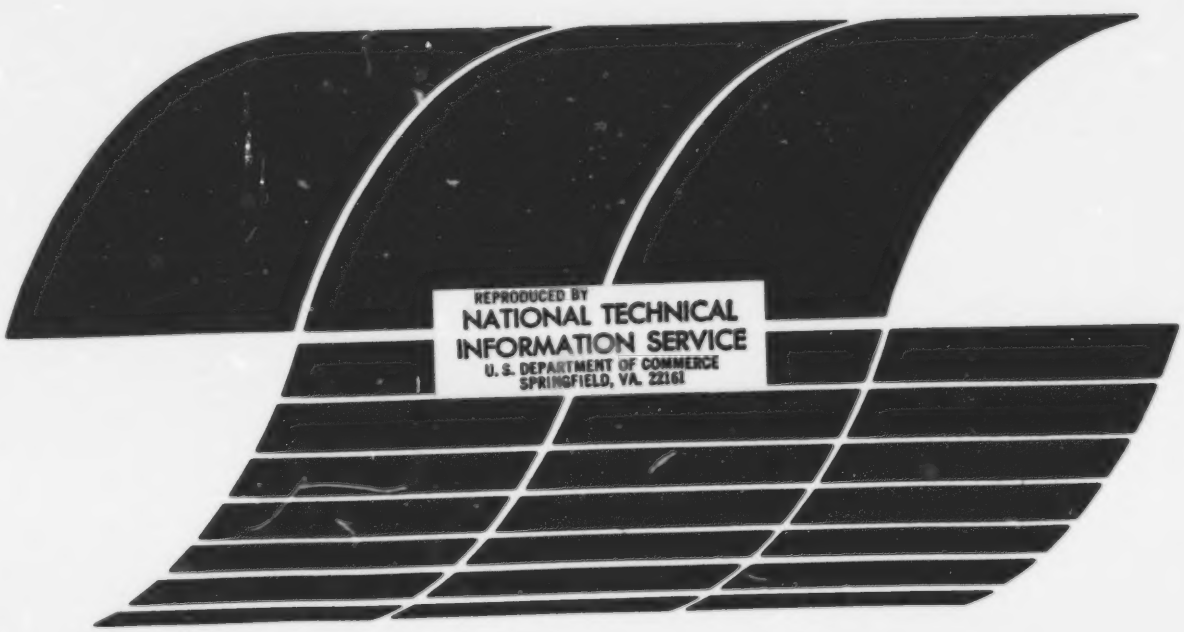

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Assessment of the Effects of Chlorinated Seawater from Power Plants on Aquatic Organisms

by

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EXECUTIVE SUMMARY

This report was prepared for the U.S. Environmental Protection Agency to provide a comprehensive review of available data on the effects of chlorinated seawater from power plants on aquatic organisms. The report is a compilation of published and unpublished research efforts, and communication with individuals currently involved in related studies. Three areas were investigated: 1) chemical characterization of power plant discharges produced by chlorinating seawater, 2) the toxicity of the compounds, identified in (1), to aquatic organisms, and 3) methods for determining the presence of chlorine and/or chlorine derived oxidants in seawater.

The culmination of this effort produced the following overall conclusions and recommendations:

- The toxicity of chlorinated seawater effluent from power plant cooling systems is due primarily to the presence of various oxidant residuals produced by chlorination rather than to just residual chlorine.
- The amperometric titration method is generally adequate to measure total oxidant residuals, (which include chlorine and bromine residuals) where identification of specific compounds is not required.
- Further studies are required to determine both individual species present in chlorinated power plant discharges and the toxicity of the identified species on aquatic organisms.
- More specific analytical procedures may be required if it is found that individual compounds are significantly more toxic at lower levels than can be measured presently.

It should be noted that each power plant presents a unique situation. Site specific parameters (such as compound in the intake water, etc.) as well as the types of aquatic life which exists in the discharge area must be considered for both analytical measurements and toxicity studies.

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SECTION 1.0
INTRODUCTION

Large volumes of cooling water are required by power plants. Often this requirement is met by locating the power plant near a major body of water. Because of the favorable conditions for aquatic organism growth within the cooling water system, most power plants are confronted with biofouling problems. Bacterial and algoid slimes, and higher order aquatic organisms often attach themselves to surfaces within the cooling circuit, thus reducing cooling system flow rates and heat transfer efficiencies. The use of chlorine has been the most common method for controlling biofouling.

Chlorine when used in this and other applications, may present toxicological problems to aquatic organisms in the receiving waters. The toxicity of chlorine and chlorination derived oxidants from power plant cooling water discharges are presently being investigated by the various researchers. The impetus for these investigations are: 1) PL 92-500 Section 307(a) of the toxic substances control act, which requires that each pollutant be individually studied, assessed and regulated and a settlement between EPA; and 2) the environmental groups relating to toxic material discharges.

This report was prepared under the direction of the EPA to provide a portion of the base from which regulations may be promulgated. The main objectives of this study are the characterization of seawater, evaluation of amperometric titration for determining residual chlorine in seawater, and the assessment of toxicity from seawater chlorination. To meet these objectives, this report includes a state-of-the-art review of available data from past studies on the aforementioned topics. In addition, current ongoing research studies investigating various aspects of the characterization of chlorinated seawater, toxicity or measurement techniques were either identified or contacted.

SECTION 2.0

CONCLUSIONS AND RECOMMENDATIONS

During the course of this study it has become evident that additional chlorinated seawater research should be initiated. This section will highlight the conclusions which were reached in each of the subject areas (chlorinated seawater characterization, amperometric titration and toxicity) and present recommendations for further research.

Conclusions

Characterization of Chlorinated Seawater

- The chemical compounds present in seawater power plant discharges are dependent upon several factors: 1) chemical species present in intake water, 2) chlorine dosage, 3) reaction duration, 4) pH, 5) temperature, and 6) light exposure.
- A complete chemical analyses of individual species present in chlorinated seawater have not been performed. The requirement for site specific information calls for each power plant discharge to be analyzed separately to eliminate potential sources of extraneous influence.
- Many of the compounds suspected or identified to be present in chlorinated seawater are either contained in the list of 129 toxic substances, or are potentially toxic although not presently included in this list.

Amperometric Titration

- The amperometric titration method is presently considered the best available method for analyzing oxidants in all water types by a majority of researchers. This method can determine chlorine residuals quantitatively, however, only in fresh water.
- Many compounds in chlorinated seawater interfere with the amperometric titrations in the measurement of free and/or combined chlorine residuals.

- Current technology indicates that the amperometric titration method can measure reliably concentration of residual oxidant up to a detection limit of 0.01 mg/l, which is half the toxicological limit identified by Mattice as causing chronic toxicity to marine organisms in power plant discharge.

Toxicity of Chlorinated Seawater

- Chlorination of seawater has been shown to cause toxic reactions in various aquatic life forms. The specific compounds causing the toxic effects, however, have not been quantified.
- Bromoform, a by-product of seawater chlorination, has been identified as a major contributor to toxicity in power plant discharges. However, preliminary assessment by various researchers indicated that bromoform may not be as toxic as chloroform because of its volatility and degradability in seawater. Further study is necessary to substantiate this claim.
- Other brominated compounds suspected to cause toxicity have not been clearly identified due to lack of specific analytical techniques.

Recommendations

- Continue research into characterization of chlorinated seawater.
- Based upon specific chemical species identified in the characterization studies, begin toxicological studies, using continuous flow-through system.
- Develop more sophisticated analytical techniques such as GC/MS which will measure quantitatively those compounds identified as toxic to aquatic organisms.
- Revise terminology used in chlorinated seawater measurements; rather than specifying free or residual chlorine measurements the appropriate terminology should be total oxidant or chlorine derived oxidants measurements instead.
- Compile and evaluate toxicity data of other biocides other than chlorine for condenser tube biofouling control.
- Conduct bench scale studies to evaluate control technologies for the removal of organics that react with chlorine to cause toxicity.

- Evaluate alternative analytical methods for chlorine residual measurement, if research indicates that chlorine residuals specifically account for the toxicity of the power plant discharge.
- Evaluate the effects of dechlorination (using sulfur dioxide or sodium sulfite) on potential toxicity reduction.

SECTION 3.0

CHARACTERIZATION OF CHLORINATED SEAWATER FROM POWER PLANTS

An important consideration in the assessment of the amperometric titration method as well as the evaluation of toxicity of chlorinated seawater is the understanding of the nature and characteristics of chlorinated seawater from power plants. To this end, the section is divided into: (1) power plant cooling system description; (2) characterization of raw seawater; (3) characterization of chlorinated seawater; and (4) comparison of identified chlorinated seawater species to the list of 129 toxic pollutants. The following is a detailed discussion on these areas.

Cooling System Description

Most power plants, whether fossil fuel or nuclear, require large amounts of water to dissipate waste heat. The source of the water used is generally nearby natural water bodies; therefore, coastal power plants usually use seawater for cooling.

The typical power plant cooling circuit is a once-through system designed for an 11°C (20°F) temperature rise across the condenser coils. This requires a water retention time of approximately 5 to 10 minutes within the cooling circuit.

The amount of water required by a once-through cooling system is dependent mainly upon the facility size in terms of gross generating capacity. Figure 1 is a graphic presentation of the approximate amount of seawater required by a once-through cooling system for power plants of various gross generating capacities. It was developed by linearizing, using the least square method, design flow rate data for several coastal power plants of different design gross generating capacities as reported by Hergot et.al. (1) and Yu et al. (2)

The inherent drawbacks of cooling systems using water from natural sources are the formation and growth of various biological species on channel walls and condenser tubes. In extreme instances this growth can cause plugging of the condenser tubes and reduces flow in the intake and

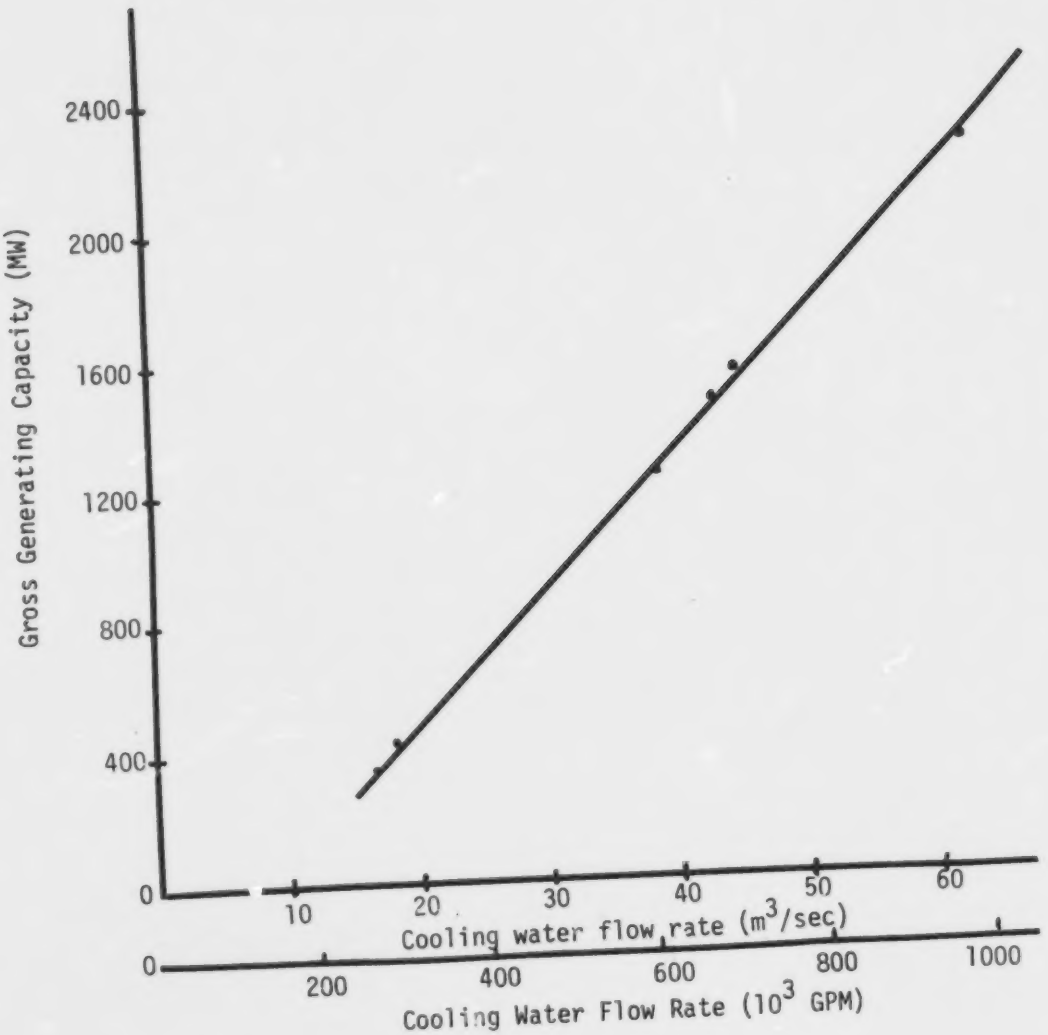


Figure 1. Approximate amount of seawater required by a once-through cooling system for steam electric power plants.

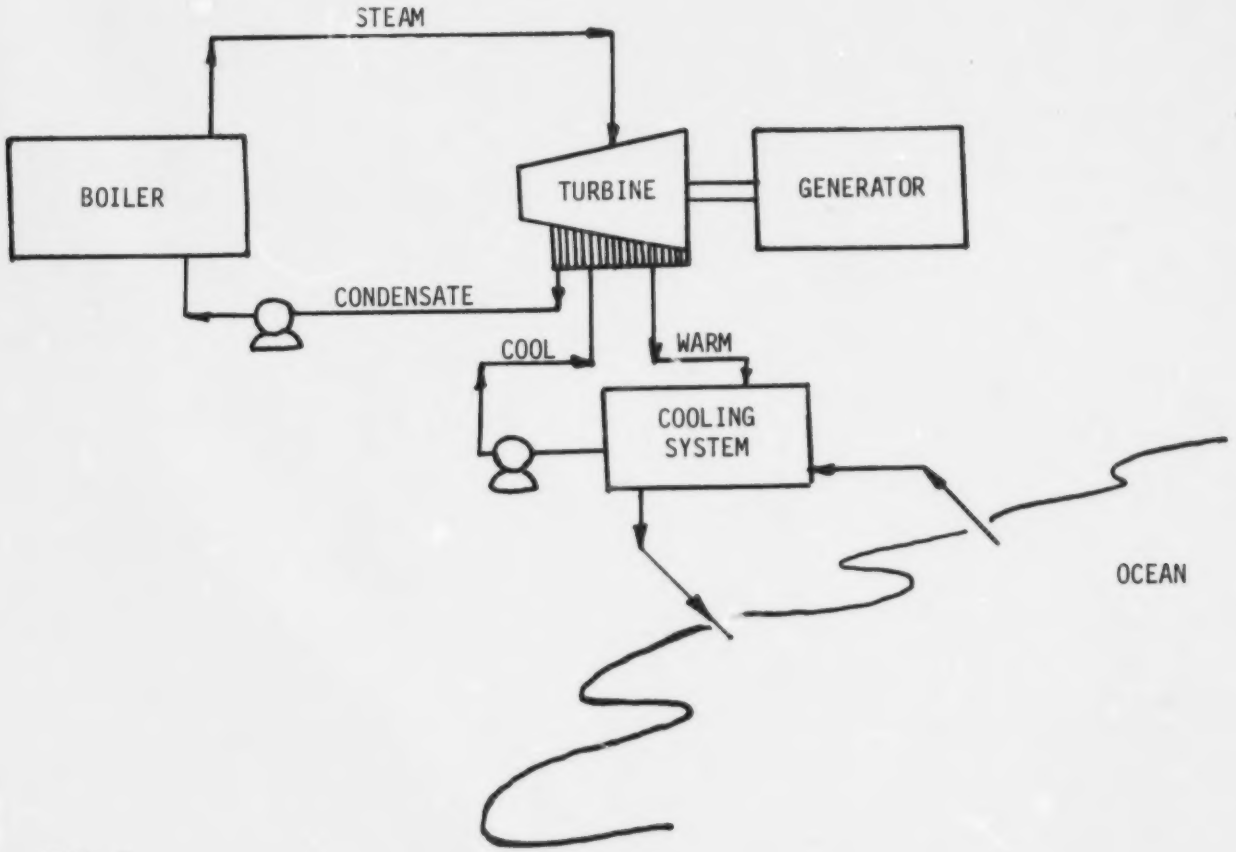
discharge channels. Conditions such as these require unit shutdown and drainage, and the chemical and/or manual removal of the fouling organism. In less severe cases biological growth in the form of slime develops on the condenser tubes, causing a degradation of the heat transfer characteristics of the condensing unit which reduces the overall generating capacity of the facility.

To counteract these problems, various methods have been used in an attempt to control and/or curtail biofouling problems. The most successful and widely applied method of biofouling control is chlorination. The first documentation of the successful application of chlorination in a commercial power plant was in 1924, and the development of high-capacity chlorination equipment commenced in 1930. Since that time chlorination for biofouling control in power plants has enjoyed widespread use.

The basic power plant consists of a boiler, turbine/generator and cooling system. A simplified diagram of this basic system is shown in Figure 2. Basically the steam/condensate loop is a closed system, and the cooling water circuit is an open loop. A simplified diagram of a typical once-through cooling system is given in Figure 3. Water from a natural water body is brought into the circuit through an intake channel; it is divided into parallel streams and then chlorinated. The chlorinated water passes through a bar rack system in order to remove large debris, such as seaweed, kelp and larger marine animals; it is pumped through the condenser and acts as a heat sink as it passes through the condensers (typical design calls for an 11°C (20°F) temperature rise. From the condenser it once again combines into a single stream and passes through a common discharge channel back to the natural water body. Table 1 gives a summary of design chlorine concentrations at the points identified as chlorine application and chlorine residue in Figure 3. The Environmental Protection Agency has established guidelines for the discharge of free chlorine to receiving water bodies; these guidelines allow 0.5 mg/l maximum and 0.2 mg/l average concentration for up to two hours per day from any one unit (3). Many state standards are more stringent than the federal standards.

Characterization of Raw Seawater

There are two basic terms used to describe seawater. The terms are salinity and chlorinity. By definition, salinity is the content of dissolved salts in seawater; and chlorinity is the content of halogen ions other than fluoride in seawater. A great deal of information about the chemical



REF. 2

Figure 2. Schematic flow diagram of power plant

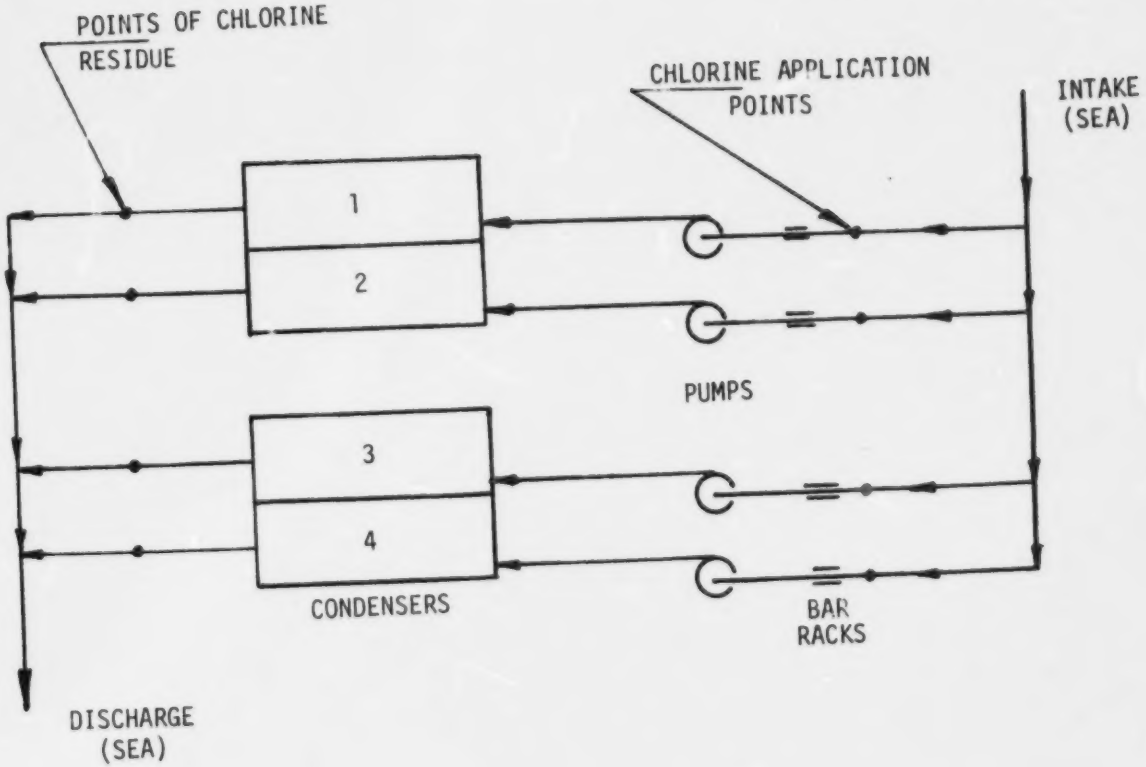


Figure 3. Flow diagram of a typical once-through cooling system using seawater

TABLE 1. TYPICAL DESIGN FREE Cl_2 AND Cl_2 RESIDUE CONCENTRATIONS

Type of Chlorination	Cl_2 Concentration at Point of Application	Cl_2 Residue Concentration Downstream of Condenser
Continuous	0.50 ppm free Cl_2*	0.25 - 0.5 ppm*
Intermittant	1.5 - 4.0 ppm free Cl_2	1.0 ppm

* Inlet water temperature greater than $277^{o}K$ ($40^{o}F$)

nature of a given water sample is conveyed by the numeric values of these terms.

The salinity of seawater varies only slightly in the major oceanic water masses throughout the world. The extreme in salinity values as identified by Todd (4) range from a low of 33.5‰ for Subartic water in the North Pacific to a high of 36.4‰ for Mediterranean water in the North Atlantic. Smith (5) presented data which indicates that the mean value of salinity for seawater is 35‰. This value will be used to normalize information which will be presented in Tables 2 through 6.

Strickland (6) discussed the Knudsen equation which establishes a relationship between chlorinity and salinity. The equation is as follows:

$$Sa = 0.030 + 1.8050\ Cl$$

where:

Sa is salinity

Cl is chlorinity

By this relationship, assuming that the salinity of typical seawater is approximately 35.0‰ then the chlorinity of typical seawater is approximately 19.4‰.

Tables 2 through 6, which are modified versions of data presented by Smith (5), give an overall characterization of the most probable components of seawater. Table 2 gives a list of eleven species which are the major ions found in seawater as well as their respective concentration ranges. The data presented is normalized to a salinity of 35‰ which corresponds (as per Knudsen equation) to a chlorinity of 19.4‰. As can be seen in the table the average value of chloride is 19.353 g/kg which corresponds to approximately 19.4‰. The data presented in this table reveals that approximately 86% of the total dissolved solids in typical seawater are sodium and chloride ions, and that approximately 98% of the total dissolved solids are made of four major ions (sodium, chloride, magnesium, and sulfate).

Table 3 presents a list of the chemical species found in seawater. It lists individual elements and then the most common chemical form in which they are found in seawater. This table shows that certain elements, such as carbon nitrogen and magnesium, are found in several forms; whereas, others, such as chlorine and bromine are typically found in only one form.

TABLE 2. CONCENTRATION OF MAJOR IONS IN SEA WATER (g/Kg SEA WATER) NORMALIZED TO 35% SALINITY

Ion	Ave. Value	Range
Chloride	19.353	
Sodium	10.76	10.72 - 10.8
Magnesium	1.297	1.292 - 1.301
Sulfate	2.712	2.701 - 2.724
Calcium	0.4123	0.4088 - 0.4165
Potassium	0.399	0.393 - 0.405
Bicarbonate*	0.145	0.137 - 0.153
Bromide	0.0673	0.0666 - 0.0680
Boron	0.0046	0.0043 - 0.0051
Strontium	0.0078	0.0074 - 0.0079
Fluoride	0.0013	0.0012 - 0.0017

* The values reported for bicarbonates are actually titrated alkalinities.

(Reference 5, page 4)

TABLE 3. CHEMICAL SPECIES IN SEA WATER

Element	Chemical Form
Hydrogen	H_2O
Helium	He(g)
Lithium	LI^+
Boron	$B(OH)_3$, $B(OH)_4$
Carbon	HCO_3^-, CO_3^{2-}, CO_2, $MgHCO_3^+$, $NaHCO_3^o$, $MgCO_3^o$, organic compounds
Nitrogen	NO_3^-, NO_2^-, NH_3, $N_2(g)$, organic compounds
Oxygen	H_2O, $O_2(g)$, SO_4^{2-}, organic compounds
Fluorine	F^-, MgF^+, CaF^+
Neon	Ne(g)
Sodium	Na^+, $NaSO_4^-$, $NaHCO_3^o$
Magnesium	Mg^{2+}, $MgSO_4^o$, $MgHCO_3^+$, $MgCO_3^o$
Aluminum	$Al(OH)_3$
Silicon	$Si(OH)_4$, $SiO(OH)_3^-$
Phosphorus	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}
Sulfur	SO_4^{2-}, $NaSO_4^-$, $MgSO_4^o$, $CaSO_4^o$
Chlorine	Cl^-
Argon	Ar(g)
Potassium	K^+, KSO_4^-
Calcium	Ca^{2-}, $CaSO_4^o$, $CaHCO_3^+$
Titanium	$Ti(OH)_4$
Vandium	$VO_2(OH)_3^{2-}$
Chromium	$Cr(OH)_2^+$, $CrOH^{2+}$, CrO_2^-, CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4
Manganese	Mn^{2+}, $MnSO_4^o$, $Mn(OH)_{3,4}$
Iron	$Fe(OH)_3$, $Fe(OH)_2^+$
Cobalt	Co^{2+}, $CoSO_4^o$

(Continued)

TABLE 3. (Continued)

Element	Chemical Form
Nickel	Ni^{2+}, $NiSO_4^o$
Copper	Cu^{2+}, $CuSO_4^o$, $CuOH^+$
Zinc	Zn^{2+}, $ZnSO_4^o$, $ZnOH^+$
Germanium	$Ge(OH)_4^o$, $GeO(OH)_3^-$
Arsenic	$H_3AsO_4^-$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}
Selenium	SeO_4^{2-}
Bromine	Br^-
Krypton	Kr(g)
Rubidium	Rb^+
Strontium	Sr^{2+}, $SrSO_4^o$
Molybdenum	MoO_4^{2-}
Silver	$AgCl_2^-$, $AgCl^{2-}$,
Cadmium	$CdCl^+$, Cd^{2+}, $CdSO_4^o$
Iodine	IO_3^-, I^-
Zenon	Xe(g)
Cesium	Cs^+
Barium	Ba^{2+}, $BaSO_4^o$
Lanthanum	La^{3+}, $La(OH)^{2+}$
Tungsten	WO_4^{2-}
Gold	$AuCl_4^-$, $AuCl_2^-$
Mercury	$HgCl_3^-$, $HgCl_4^{2-}$
Thallium	Tl^4
Lead	Pb^{2+}, $PbSO_4^o$, $PbOH^+$
Radon	Rn(g)
Radium	Ra^{2+}, $RaSO_4^o$
Uranium	$UO_2(CO_3)_3^{4-}$

Table 4 gives a list of major chemical species found in seawater, and the probability of their occurrence given their elemental composition. This table in conjunction with Table 2 can be used to determine the mass of a given chmical species per unit mass of seawater, e.g., there would be approximately 0.64 g of $MgSO_4$ in each kilogram of seawater. In Table 5 a list of minor constituents found in seawater and their respective concentration ranges, as well as, average concentrations are presented. These constituents are listed in the elemental form, and it is expected that all of these together will make up less than 1% of the total dissolved solids in seawater.

Table 6 provides a list of dissolved organic substances found in seawater and their expected concentration ranges. Because of the large number of organic compounds that are present in seawater, rather than identifying each compound, it was decided, for the sake of brevity, to list only major classes of organic species and the cumulative concentration of each class.

In his discussion of the character of seawater, Liptak (7) noted that there is a difference between open ocean and coastal seawaters. In the open ocean intense density stratification exists which hampers mixing between surface and deep waters. Because of this the cycling of nutrients is hindered (thus reducing biological activity). Whereas, in coastal waters, because of shallow bottoms and constant tidal and wave activity, a great deal of mixing occurs, which stimulates the cycling of nutrients. It is this cycling of nutrients and an abundance of suspended materials which provide an environment conducive to active biological formation and growth. The presence of abundant aquatic life forms plus the conditions common to power plant cooling systems, such as increased ambient temperatures and large surface areas available for organism attachment, create an environment which stimulates the occurrence of biofouling problems.

Characterization of Chlorinated Seawater

According to Sugam et.al. (8) when seawater is chlorinated, the principle equilibrium species formed are brominated compounds analogous to chlorinated species produced in fresh water. In the pH range from 6 to 8 these brominated species are HOBr, OBr^-, NBr_3, $NHBr_2$, and NH_2Br. The formation of these species occur because the bromide (Br^-) present in seawater is readily oxidized by chlorine.

TABLE 4. THE MAJOR CHEMICAL SPECIES IN SEA WATER[5]

Constituent	Percentage of Constituent present as each species @ 25°C, 19.375‰ Chlorinity, 1 atm., and pH 8.0
Chloride	
Sodium	Na^+ (97.7%); $NaSO_4^-$ (2.2%); $NaHCO_3^o$ (0.03%)
Magnesium	Mg^{2+} (98%); $MgSO_4$ (10%); $MgHCO_3^+$ (0.6%); $Mg\ CO_3^o$ (0.1%)
Sulfate	SO_4^{2-} (39%); $NaXO_4^-$ (37%); $MgSO_4^-$ (19%); $CaSO_4^o$ (4%)
Calcium	Ca^{2+} (88%); $CaSO_4^o$ (11%); $CaHCO_3^+$ (0.06%); $CaCO_3^o$ (0.1%)
Potassium	K^+ (98.8%); KSO_4^- (1.2%)
Bicarbonate	HCO_3^- (64%); $MgHCO_3^+$ (3%); CO_3^{2-} (0.8%); $MgCO_3^o$ (6%); $NaCO_3^-$ (6%); $NaCO_3^-$ (1%); $CaCO_3^o$ (0.5%)
Bromide	--
Boron	$B(OH)_3$ (84%); $B(OH)_4^-$ (16%)
Strontium	--
Fluoride	F^- (50 - 80%); MgF^+ (20 - 50%)

TABLE 5. MINOR CONSTITUENTS OF SEA WATER* (μg/liter)[5]

Constituent	Average Value	Range
Rubidium	120	89 - 134
Aluminum	2	0 - 7
Lithium	185	180 - 190
Barium	20	5 - 93
Iodine	63	48 - 80
Silicon	2000	0 -4900
Nitrogen	280	0 - 560
Zinc	6.5	1 - 48.4
Lead	0.05	0.02 - 0.4
Selenium	0.2	0.052 - 0.50
Arsenic	0.46	0.2 - 35
Copper	2	0.2 - 4
Tin	0.8	--
Iron	6.6	0.1 - 62
Cesium	0.4	0.27 - 0.58
Manganese	1.5	0.2 - 8.6
Phosphorus	30	0 - 90
Thorium	0.05	$2 - 40 \times 10^{-4}$
Mercury	0.03	--
Uranium	3	2 - 4.7
Cobalt	0.27	0.035 - 4.1
Nickel	5.4	0.43 - 43
Radium	8×10^{-8}	$4 - 15 \times 10^{-8}$
Beryllium	5.7×10^{-4}	--
Cadmium	0.113	0.02 - 0.25
Chromium	0.3	0.23 - 0.43
Titanium	1	--

* Excluding dissolved gases

TABLE 6. DISSOLVED ORGANIC COMPOUNDS IN SEA WATER[5]

	Constituent	Range
1.	Carbohydrates	0.2 - 8.4 mg/l
2.	Proteins and Their Derivatives - Total	14.9 - 156.5 µg/l
	• Polypetides and Polycondensates	6.9 - 39.1 µg/l
	• Free Amino Acids	8.0 - 117.4 µg/l
3.	Aliphatic Carboxylic and Hydroxycarboxylic Acids	0.44 - 4.71
4.	Biologically Active Compounds	1.8 - 36.64 mµg/l
5.	Humic Acid	Present
6.	Phenolic Compounds	3 - µg/l
7.	Hydrocarbons	Traces

Sugam further indicated that when chlorine in the form of hypochlorous acid (HOCl) is added to seawater the oxidation of bromide would occur instantaneously as shown in the following exchange reaction:

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$

Carpenter et.al. (9) in their discussion of the reactions of chlorine with seawater presented the following chemical equations to describe the decay of gaseous chlorine to chloride ions. When gaseous chlorine (Cl_2) is added to seawater the following hydrolysis reaction would occur:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

Gaseous chlorine may further react with the bromide in seawater to produce the following sets of reactions (9):

$$2Br^- + Cl_2 \longrightarrow Br_2 + 2\,Cl^-,$$
$$Br_2 + H_2O \longrightarrow Br\,OH + H^+ + Br^-$$
$$BrOH + Cl_2 \longrightarrow BrCl + HOCl;$$

and

$$3\,BrOH \longrightarrow BrO_3^- + 3H^+ + 2Br^-,$$
$$BrCl + 2Cl_2 \longrightarrow Br\,Cl_5,$$
$$BrCl_5 + 3\,H_2O \longrightarrow BrO_3^- + 6H^+ + 5\,Cl^-.$$

In discussing the environmental toxicity of chlorine the common unit of measure is "Free Available Chlorine" (FAC). For hypochlorous acid this unit FAC can be represented as follows (10):

$$FAC = HOCl + OCl^-$$

Johnson (10) stated that in seawater at pH 7.5 and temperature of 298°K (77°F) the FAC is approximately half HOCl and half OCl^-, and that as the pH increases to create more basic solution, the FAC shifts towards the hypochloride ion (OCl^-).

The brominated species formed in seawater given the above equilibrium shift is shown in the following equation (9).

$$Br^- + 3\ ClO^- \longrightarrow BrO_3^- + 3\ Cl^-$$

Johnson (11) in discussing the chlorination of seawater stated that chlorine would react with the bromine present in natural seawater to produce HOBr; likewise, the chlorine would react with the iodide present in natural seawater to produce HOI. These reactions will go to completion rapidly, in addition, further oxidation of these two species will occur resulting in the rapid formation of IO_3^- and the slower formation of BrO_3^-.

In the presence of ammonia, bromine formed during the oxidation of bromide by chlorine or chloramines will react with ammonia to form bromamines. The relative quantities of bromamines and chloramines are kinetically rather than equilibrium controlled. Because the presence and formation of these haloamines are a function of reaction kinetics, the predominate chloramine is monochloramine (NH_2Cl) and the predominate bromamines are dibromamine ($NHBr_2$) and tribromamine (NBr_3) (10). Sugam and Helz (8) reported that the conversion of HOCl to HOBr in seawater, in the absence of amino-nitrogen, reaches 99% completion in less than 10 seconds at pH 8; at lower pH it reaches completion even more rapidly. Therefore, if a total conversion of chlorine to bromine is assumed, Figure 4 shows that the distribution of bromine species present in seawater is a function of both pH and the logarithm of the initial mole ratio of ammonia to bromine. The data presented identifies species which will be present after 1 to 2 minutes of contact time and the lines indicate equal equivalent concentrations (1).

Figure 5 is similar to the chart developed by Davis et.al. (12) to present the theoretical degradation of chlorine as a result of chlorinating natural seawater. The decay of diatomic chlorine gas occurs between levels I and II; this reaction occurs rapidly and goes to completion within a few seconds after the addition of chlorine. Between levels II and III the chemical composition and abundance of products formed is a function of the physical and chemical parameters of the water, including, but not limited to, temperature, pH, ammonia, and bromine available as reaction components. Species found in level IV include halogenated organic constituents which may be formed at either level II or III or both.

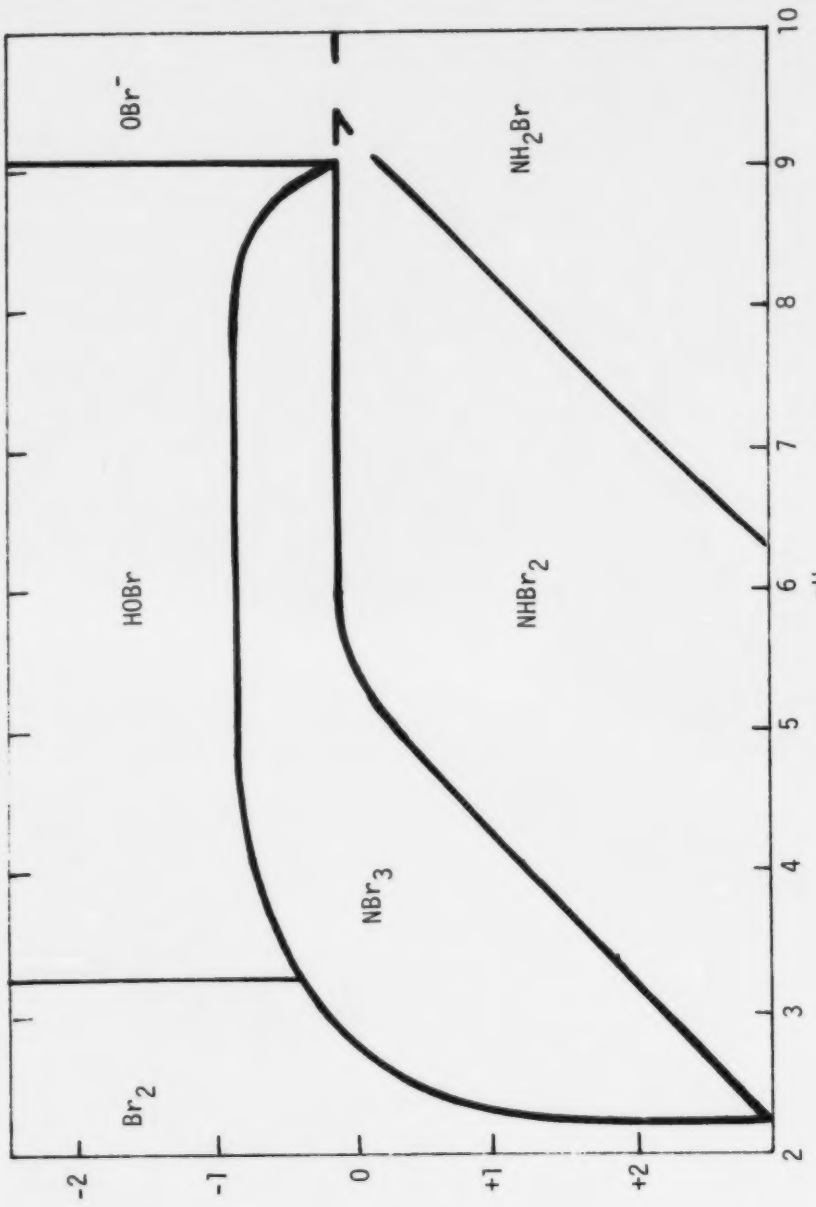


Figure 4. Principle species of bromine and bromamine

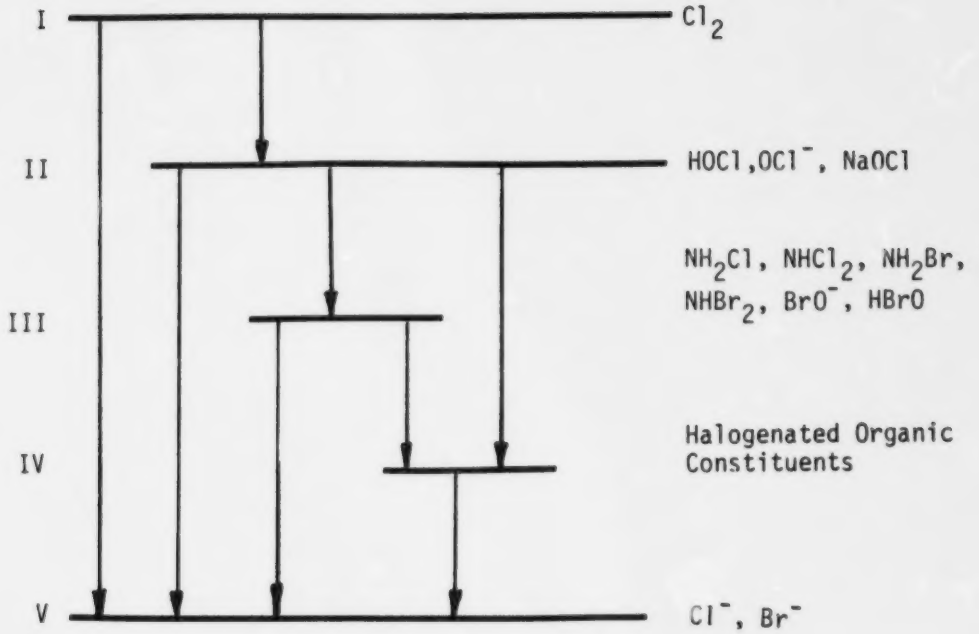


Figure 5. Degradation processes for chlorine in saline waters

A charge balance results as one atom of Cl passes from level I to V for each atom of Cl that passes from level I to II, or in reduction or replacement reactions in which Cl^- is released at any of the other levels between I and V.

In their discussion of the reaction of chlorine upon various organic species Jolley et.al. (13) presents several chemical equations to describe the formation of various chlorinated hydrocarbons. Portions of their work is presented in the following narrative.

When chlorine reacts with organic substances such as proteinaceous material, found in bacterial cell walls, a chlorine substitution reaction can occur leading to the formation of N-chlorinated proteinaceous material. If the organic substance involved in this substitution reaction is an amine the reaction formula will appear as follows:

$$R\text{-}NH_2 + HOCl \longrightarrow R\text{-}\overset{H}{N}Cl + HOH$$

Likewise, if the organic substance involved is an amide the reaction formula will appear as follows:

$$R - \overset{O}{\overset{\|}{C}} - NH_2 + HOCl \longrightarrow R - \overset{O}{\overset{\|}{C}} - \overset{H}{N}Cl + HOH$$

The kinetics of the formation of the N-chloro compounds is considerably slower with amides than with amines.

The major portion of soluble organic matter in cooling water is made up of humic material. Humic material is a generic type of organic substance which is classed according to solubility. These materials are complex polymers which range in molecular weight from several hundred to many thousand grams per mole. They are made up of various aromatic and alicyclic noieties containing alcoholic, carbonyl, carboxylic, and phenolic functional groups. Phenols and aromatic acids are readily chlorinated in aqueous solutions by HOCl or OCl^-. Chlorine substitution reactions with phenolic compounds and aromatic organic acids are shown in Figure 6.

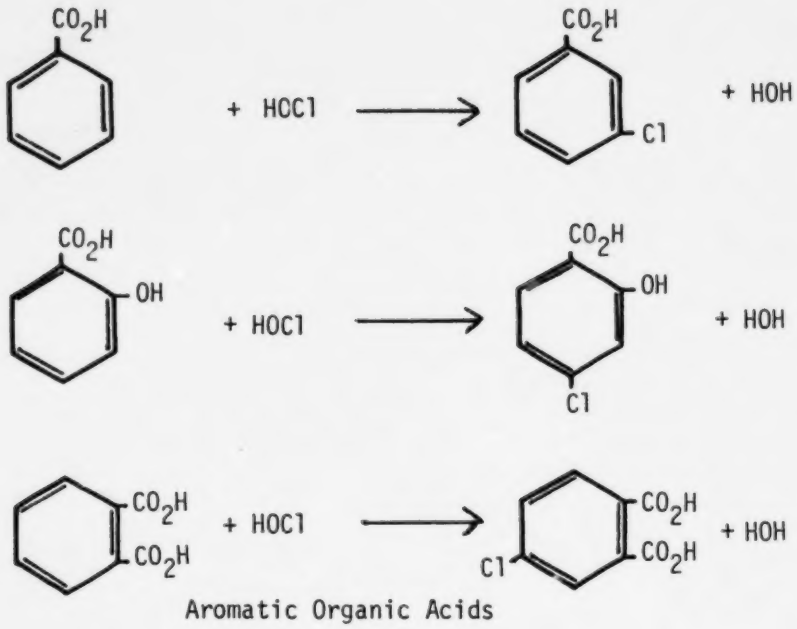
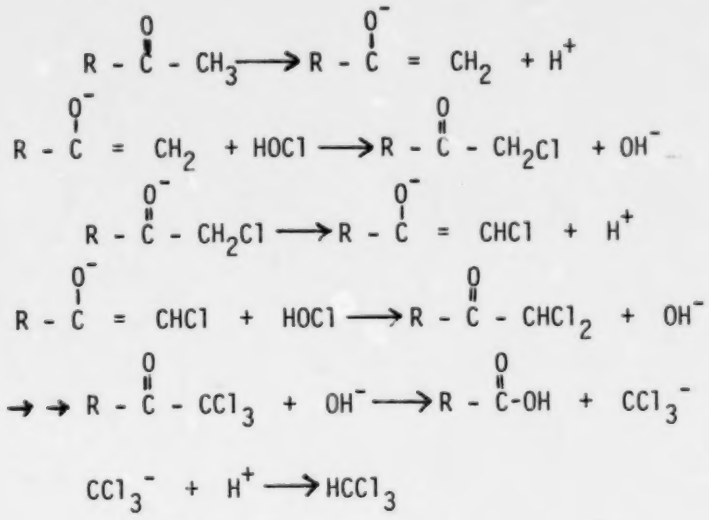


Figure 6. Chlorine substitution reaction

A possible pathway for chlorine substitution reactions with humic material is the haloform reaction. This reaction appears as follows:



If the haloform reaction is the primary path of chlorine substitution with humic material the principle organic species contained in chlorinated seawater would in all probability be chloro-organics such as chloroforms (13). In seawater containing significant quantities of bromide ions (67 mg/l), humic material will react more preferentially with the bromide ions to form bromo-organics, thus impeding chloroform formation. Since HOCl is readily converted to HOBr in the presence of bromide ions little or no chloroform is expected to occur in chlorinated seawater. The mechanisms by which bromoform is produced is not well understood; however, reactions similar to those postulated for chloroform formation are likely to occur. The predominant species identified by Carpenter and Smith (14) are bromoform and, to a lesser extent, chlorodibromomethane. According to these authors, the presence and intensity of light and particulates will affect the production of bromoform; whereas temperature does not appear to be a variable.

Comparison of Identified Chlorinated Seawater Species to the list of 129 Toxic Pollutants

Data presented in previous sections of this document indicate that when chlorine is added to seawater, bromide present in the seawater is oxidized by the chlorine and the resulting species formed are brominated compounds analogous to chlorinated species found in fresh water. In addition to these

compounds, which are formed by replacement reactions, are a wide variety of other species formed by a number of different types of reactions. These reactions and the compounds formed are dependent on the presence of various contaminants and/or pollutants in the intake water; therefore, the composition of the chlorinated discharge water is to a large degree dependent upon the composition of the original intake water. This fact in itself implies that the composition of chlorinated discharge water is site and time specific. Some of the more typical compounds that may be found in the chlorinated discharge waters are bromamines, chloramines, chloroforms, bromaforms, and halogenated organic compounds.

An example of the complexity of predicting and/or evaluating the constituents found in chlorinated sea water can be shown by observing the reaction modes and compounds formed in sea water containing N-halamines. Kovacic et.al. (15) in their studies of N-halamines, such as N-bromamines and N-chloramines, indicate that they may act as a stimuli for the formation of various classes of organic compounds. They attributed this to the fact that the nitrogen and halogen act as sites for chemical reactions and that these reactions can occur in quite diverse manners.

Examples of the diverse reaction modes are as follows (15):

- The nitrogen component may act as a cation (bicyclic rearrangement), anion (hydrazine formation), radical (photolysis and addition alkanes), radical cation (Hoffman-Loffer reaction), and a base (nucleophilic substitution).
- The halogen component may act as a cationic (halogenation), anionic (Grinard reaction), and radical (photolysis).
- When N-H is present reactions which are typical to this structure may also be observed.

The organo-chlorides formed by reactions such as those shown in Figure 6 are included in the list of 129 priority pollutants. These priority pollutants which include chlorinated species of benzene, ethane, ether, and phenol to name a few, could as Jolley et.al. (13) suggests be readily formed in a chlorinated aqueous solution provided the parent organic species are present. Various organo-bromides analogous to these organo-chlorides may also be formed. The formation of such species may, as Kovacic et.al. (15) suggest , result because of the presences of organic halamines. The brominated species do not enjoy the notoriety that organo-chlorides have received; however, they may be as toxic.

At this time no quantitative studies of chlorinated seawater have been completed. Therefore, any prediction of exact compounds and their respective compositions would include a great deal of supposition. However, given the proper intake conditions any one or a number of substances contained in the list of 129 toxic pollutants may occur or exist in chlorinated discharge water from power plant cooling systems. A preliminary qualitative characterization of compounds found in chlorinated seawater was conducted by Bean et.al. and is presented in Section 5.0 under the heading of "Identification of Potentially Toxic Species".

SECTION 4.0

EVALUATION OF AMPEROMETRIC TITRATION FOR DETERMINATION OF RESIDUAL CHLORINE IN SEAWATER

The determination of free and combined chlorine has historically been done with applications in drinking and waste waters. The requirements and problems associated with monitoring chlorine residuals in power plant cooling waters are considerably more complex. This is particularly true when seawater is used as the coolant. The chemistry of chlorine in seawater shows little resemblance to that of either fresh or waste waters.

A number of methods for determining chlorine residuals are available. The most widely accepted is the amperometric titration method. This method for the determination of free available chlorine and combined chlorine species in water has been considered the standard for many years. Since it was first reported by Marks and Glass (16) in 1942 it has become the most widely used method for chlorine determination (17,18). Recently the amperometric titration method has become suspect when used for chlorine determinations in seawaters (11,19).

This section provides; (1) a general discussion of the amperometric titration method; (2) a brief discussion of iodine chemistry as it relates to chlorine determinations in seawater; and (3) an assessment of the methods accuracy, precision and interferences when used in seawater determinations. Areas where further research is required and a brief discussion of alternative methods is also included.

General Method Description

Amperometric titration has been used to determine total residual chlorine and also to differentiate between free and combined available chlorine in all types of waters. Two slightly different techniques are employed; a forward titration (generally considered the standard), and a backward titration. The difference is in the order of chemical additions. In the back titration, phenylarsineoxide (PAO) is added in excess and a biiodate solution is used as the titrant; whereas in the forward titration biiodate is added

in excess and PAO is used as the titrant. This section will deal only with the standard forward titration method. The interferences and limitations are similar between the two methods.

The principle of amperometric titration is an adaptation of polarographic principles. When the cell of the titrator is immersed in a sample containing chlorine or other oxidants, current is generated; but as phenylarsine-oxide is gradually added, the chlorine is neutralized and the generation of current ceases. The determination of free available chlorine is done between pH 6.5 and 7.5. In this pH range reaction of combined chlorine is slow. For the determination of combined chlorine, potassium iodide (KI) and buffers are added in the proper amount to buffer the solution to pH 3.5 to 4.5 and activate the slower reacting species. Monochloramines react more readily than dichloramines; this tendency provides a means for determining the two species. The addition of a small amount of KI (in the neutral pH range) enables an estimation of monochloramine concentration. Reducing the pH to the acid range while increasing the KI concentration allows for the separate determination of dichloramine content.

Phenylarsine oxide (PAO) is used as the reducing agent (the titrant in forward titrations, and added in excess in back titrations) for free chlorine or I_2 determination by the following reactions (20):

$$C_6H_5AsO + Cl_2 + 2H_2O \longrightarrow C_6H_5AsO(OH)_2 + 2HCl$$

$$C_6H_5AsO + I_2 + 2H_2O \longrightarrow C_6H_5AsO(OH)_2 + 2HI$$

The PAO is stable even in dilute solutions. A special amperometric cell is used for detection of the end point. The cell unit is connected to a microammeter and recorder for end point determination. The cell unit generally consists of a noble metal electrode and reference electrode.

Numerous variations of amperometric titration setups are in use in different labs or produced by different instrument manufacturers. Instrument manufacturers have provided automated titration apparatus for the chlorine determination for many years. Primary application has been to drinking and waste waters. The analytical requirements are for the measurement of minimum chlorine residuals in drinking and waste waters as applied to disinfection. Power plants cooling waters however, are required to be monitored for maximum chlorine residuals for the protection of aquatic organisms near the discharge point. This fact makes it necessary for power plant monitors to analyze chlorine residuals more accurately at lower levels.

Iodine Chemistry

The use of iodide salts in the determination of chlorine species is primarily to catalyz normally sluggish or negligible response to certain oxidant fractions. The salts are also employed to control ionic strength, to retard volatilization, or to serve other functions. The iodide salts are used in all the generally accepted analytical methods. Therefore, errors introduced by imperfect iodine behavior will effect all methods.

The generalized iodide - halogen produced oxidant reaction can be written as:

$$R\text{-}X + 2I^- + H^+ \longrightarrow I_2 + R - H + X^-$$

where X represents a halogen atom. For strong oxidant (e.g., HOCl, HOBR or NH_2 Cl) the reaction proceeds to the right even at neutral pH. For more inert oxidant (e.g., $NHCl_2$) the reaction is accelerated only by the addition of I^- and H^+ ions. It is this principle which allows for the selective determination of different oxidant fractions.

It is important to note that all bromine oxidant species, which may be present in chlorinated seawater, are unstable with respect to the iodine species. They are all capable of reacting quantitatively with I^- to form I_2, I_3^- and IO_3^-, although the reaction rates for several oxidant species conversions are not known. The relative concentrations of iodine species is represented by the following equation:

$$I_2 + I^- \longrightarrow I_3^-$$

In amperometric titrations this is extremely important because the electrode is most sensitive to I_2 (21).

Many potential sources of error may enter into the analysis of chlorine produced oxidants at low concentrations due to iodide reactions with chlorinated seawater. Among these potential sources of error are: those from naturally occurring iodate in the seawater; other oxidants; volatilization and reaction with organic matter. Only the first two will be discussed here. Volatilization is considered a technique error and can be minimized by proper handling and prompt analysis of the sample. Organic matter is a more common interference in wastewaters than in seawater.

Natural seawater contains about 0.06 mg/l of elemental iodine. Fresh water lakes and rivers contain considerably less (on the order of 0.002 mg/l). Wong and Brewer (22) have reported that the primary iodine species in oxygenated surface seawater is IO_3^-. Thus if the analysis is performed by a method which measures IO_3^-, then a background level will be measured. In the case of amperometric titration IO_3^- is too inert to be detected, however, when the KI solution is added the IO_3^- will react to form I_2 which will be detected. Fabian (23) and Carpenter, et.al. (19) both report this occurrance and Fabian presents rate equations for the reaction.

There are many potentially interferring oxidants which can occur in chlorinated seawater. Table 7 lists some of these. Fortunately these will react only slowly under normal analytical procedures. However proper techniques must be employed at all times if gross interferences are to be minimized.

TABLE 7. POTENTIAL INTERFERRING OXIDANTS

$S_2O_8^{2-}$	$BrCl_2$
H_2O_2	NBr
MnO_4	Br_2
HOBr	$NHBr_2$
OBr^-	NH_2Br
BrO_3^-	HNO
MnO_4^-	Cu^{+22}
MnO_2	Fe^{+3}
$BrCl_2^-$	

Limitations and Interferences

The limitations and interferences to which the amperometric titration method is subject are dependent upon the specific chemical species present in the water being analyzed. The species which may be found in chlorinated seawaters have been identified in Section 3.0. Those interferring compounds associated with the iodide chemistry have been discussed in the preceding paragraphs. This section consists of a review of the accuracy and precision of the method; the specific chemical interferences; the mechanisms by which they affect the determination and the specific interferences as they relate to seawater chlorination.

Accuracy and Precision

The amperometric titration method requires a high degree of operator skill for accurate results. The method is susceptible to mechanical as well as chemical interferences. Crecelius, et al., (24) in an as yet unpublished study, reports errors caused by different methods of handling and treating samples. The order of addition of chemicals was of major significance in introducing errors to the analysis. Crecelius recommended the mixing of KI with buffer before addition of the sample. Other mechanical errors may be introduced by exposure to light and volatilization of sample and reagents. These all may be minimized by proper analytical techniques and careful and prompt analysis of the sample.

Due to the highly unstable nature of chlorinated water samples only limited testing of the procedure by multiple laboratories have been undertaken. One such study, reported in Standard Methods (17), involved the shipping of solid synthetic unknowns. The individual laboratories mixed the solids following instructions and then immediately performed the analysis. Results of this study (which involved only fresh water and therefore should be considered to represent the best accuracy and precision obtainable by the method) indicate that the relative error, between laboratories, for the determination of free chlorine was 25% and for total available chlorine was 8.5 to 8.8%. Standard deviations, among the laboratories were 42.3% for free chlorine and 12.5 - 24.8% (dependent upon concentration) for total available chlorine. These values were for levels of chlorine from 690 to 1830 µg/l. Components present in chlorinated seawaters which cause interference to the

method may act to both reduce efficiency and increase the standard deviation.

Several alternative methods exist for the determination of chlorine, some of these methods are: chlorine flux monitor, membrane probe amperometry, specific ion electrode, iodometric methods, DPD (and other colorimetric methods) and others. Each is considered less accurate or reliable than the amperometric titration method. The DPD-Ferrous titrimetric method has been mentioned as valuable in that it detects only free chlorine. However, in seawater where Br^- is present, this selectivity is reduced. It may not, by present analytical methods, be possible to determine only free chlorine residuals in seawater.

Further research into the accuracy and precision of amperometric titration, and other analytical methods, are required. Studies specifically directed to monitoring chlorine in seawaters are needed, and only recently have programs been undertaken. A report, prepared for EPRI by the Public Service Electric and Gas Company and the University of Maryland, which is near release, looks critically at many of these methods as they relate to seawater. In addition, a recent study, currently under investigation by the power industry, evaluates the accuracy and precision of the amperometric titration method at four selected power plants utilizing different types of waters for cooling. Two of these cooling waters are from fresh water sources; one from esturine waters; and one from seawaters. Eight to ten participants, all using their own amperometric instruments, are analyzing identical samples at each of the four sites. Data are currently being compiled and, unfortunately, are not available for incorporation in this report. The development of more precise methods for chlorine determinations are also necessary if it is concluded that chlorine is the major toxic material needing monitoring. Section 5.0 of this report presents toxicological data and makes some recommendations as to which compounds are toxic and at what levels.

Chemical Interferences

Standard Methods (17) identifies compounds which interfere with the analysis of chlorine compounds by the amperometric titration method. The interferences identified are for fresh or wastewaters and do not include

compounds found in seawater. Accurate determinations of free chlorine are not obtainable in the presence of nitrogen trichlorine (NCl_3) or chlorine dioxide (17). Both of these species titrate partially as free chlorine. NCl_3 also titrates partially as dichloramine causing positive errors to both these fractions. Seawater nitrogen however, is rarely in the form of NCl_3. During each determination organic chloramines are also partially titrated. Mono- and di-chloramines interfere in a positive manner with each other (17).

Copper and silver (as sulfate and ions respectively) can cause interference. Copper interferes by plating out on the electrodes and has been noticed after heavy copper sulfate treatment in reservoirs. Silver ions act to poison the electrode (17). Concentrations of these metals in seawater are generally very low, thus have little interference.

At pH 7 and no KI (the conditions traditionally used for free chlorine determinations) other free halogens, specifically bromine are detected. Because seawaters contain relatively high concentrations of bromide ions, which when chlorinated form free bromine, this is of major importance (25). At these conditions bromamines and H_2O_2 give non-quantitative responses also (25). Bromamines are common chlorinated seawater constituents where amines are present in feed waters. The bromamine reaction in the titration is relatively slow; this may reduce the interference and accounts for the non-quantitative nature of the interference. The presence of H_2O_2 has not been confirmed in any significant quantities however.

Other compounds which have been reported to cause interferences include $Br\ O_3^-$ and $Cl\ O_3^-$. These give non-quantitative results at pH 4.2 with 250 mg/l KI added. Free bromines, chlorine, chloramines, bromamines and H_2O_2 are also determined (25). The non-quantitative nature of many of these interferences make them impossible to remove.

Interferences Particularly Related to Seawater

Many of those compounds identified in Section 3.0 as typical of chlorinated power plant seawaters are also compounds which interfere with the amperometric titrations. Some of these, specifically bromamines, are the dominant species in chlorinated seawaters. These interferences make it impossible to clearly separate free chlorine and bromine from the interfer-

ring species. The non-quantitative nature of these interferences make even the determination of total oxidant by the amperometric titration method a formidable task.

The data available on the amperometric titration method, as it is applied to determinations in seawater, does not allow for quantitative determinations of accuracy and precision. There are at present no accepted methods for eliminating the effects of the interferring compounds. It is likely that totally new procedures will need to be developed if the acutal quantities of free chlorine residuals need be known. Section 5.0, which discusses the toxicity of various compounds from chlorination of seawater, indicates that many other compounds are also toxic. The amperometric titration method may be sufficient to determine levels of total oxidants (primarily bromine and halogenated amines) that are potentially toxic in cooling water discharges. These values, however, should not be confused with free chlorine residuals.

SECTION 5.0

TOXICITY OF COMPOUNDS FORMED BY CHLORINATION OF SEAWATER

This section identifies and discusses the various chemical species formed, their relative toxicities, and the specific marine organisms affected by the addition of chlorine to seawater. Particular emphasis is placed on those chemical species identified as typical of or likely to be present in power plant cooling water discharges as delineated in Section 3.0.

Definition of Toxicity

Prior to introducing and discussing toxicity it is necessary to become familiar with the terminology commonly used in the field of toxicology. There are several ways to define and categorize toxic effects, as well as, a number of techniques used for conducting toxicity tests. Likewise, the results of these toxicity tests are expressed several different ways. The following tables: 8, 9, and 10, originally presented by Burton (26), summarizes the most commonly used methods of categorization, testing technologies and the terminology used to report results.

Table 8 identifies the general categories of toxic effects. By simplifying the information contained in this table it is possible to form two general categories of toxic effects:

- Acute toxicity which is generally lethal
- Chronic toxicity which may be either lethal or sublethal.

The other categories listed are used more as descriptive words to identify the degree and effects of toxicity on the test organism.

TABLE 8. GENERAL CATEGORIES OF TOXIC EFFECTS

Acute - involving a stimulus severe enough to bring about a response speedily, usually within two to seven days for fish.
Subacute - Involving a stimulus which is less severe than an acute stimulus, which produces a response in a longer time, and may become chronic.
Chronic - involving a stimulus which is lingering or continues for a long time, often used for periods of about one tenth of the life span or more.
Lethal - causing death, or sufficient time to cause it, by direct action.
Sublethal - below the level which directly causes death.
Cumulative - brought about, or increased in strength, by successive additions at different times or in different ways.
Delayed - symptoms do not appear until an appreciable time after exposure; often the response is triggered by occurrence of some other stress.
Short-term - acute but more indefinite
Long-term - chronic but more indefinite.

Table 9 gives the four techniques generally used for conducting toxicity tests. These are laboratory tests that may or may not produce similar results as in a natural marine environment. It is recommended that only the continuous flow or flow-through technique be used for chlorine toxicity studies with macroinvertebrates and fishes, with exception to chlorine decay studies where exposure periods are relatively short.

TABLE 9. TECHNIQUES GENERALLY USED FOR CONDUCTING TOXICITY TESTS

Static Technique - test solutions and test organisms are placed in test chambers and kept there for the duration of the test.
Static Recirculation Technique - similar to the static technique except that each test solution is continuously circulated through an apparatus to maintain water quality by such means as filtration, aeration, sterilization and returned to the test chamber.
Static Renewal Technique - similar to the static technique except that the test organisms are periodically exposed to fresh test solution of the same composition usually once every 24 hours by transferring the test organisms from one test chamber to another.
Continuous Flow or Flow-Through Technique - test solutions flow into and out of the test chambers on a once-through basis for the duration of the test. Two procedures can be used: (1) large volumes of the test solutions are prepared before the beginning of the test and these flow through the test chambers and (2) fresh test solutions are prepared continuously or every few minutes in a toxicant delivery system.

Table 10 presents the terminology most commonly used for expressing the results of toxicity tests. It should be noted that time and concentration are inseparably linked in toxicity tests; hence, time should be stated in order to give meaning to the toxicity data being reported, e.g. 24-h LD50, which is the dose of a toxicant which is lethal to 50% of the test organisms in 24 hours. The ILC50 term is ambiguous and should incorporate two additional terms to fully express the test results, e.g. 96-h ILC50 (3,180) where the 3 would represent the number of exposures and the 180 would be the total exposure time.

TABLE 10. TERMINOLOGY USED FOR EXPRESSING RESULTS OF TOXICITY TESTS

LC50 - median lethal concentration of a toxicant in solution which is lethal to 50% of the test organisms.

LC50 - median effective concentration of a toxicant in solution at which a response other than death occurs to 50% of the test organisms.

LD50 - median lethal dose of a toxicant within the organism which is lethal to 50% of the test organisms.

ED50 - median effective dose of a toxicant within the organism at which a response other than death occurs to 50% of the test organisms.

LT50 - median lethal time. Used for mortality time in fixed concentrations.

ET50 - median effective time. Used for response time other than death in fixed concentrations.

TL_m, TLm, TL_{50}, TL50 - median tolerance limit. Term used primarily by U.S. pollution biologist. Equivalent numerically to LC50.

LL50 - median lethal level. For tests which yield mortality data where neither concentration or dose applies, e.g. tests with temperature.

EL50 - median effective level. For tests which use a response other than death where neither concentration or dose applies, e.g., tests with temperature.

ILC50 - intermittent lethal concentration of a toxicant in solution which is lethal to 50% of the test organisms during intermittent exposure tests.

(Continued)

TABLE 10. (Continued)

Other terminology - usually used to describe the concentration at which toxicity ceases or the point beyond which 50% of the population can live for indefinite time:

- Incipient lethal level
- Ultimate median tolerance limit
- Lethal threshold concentration
- Median threshold concentration
- Asymptotic lethal concentration
- Asymptotic threshold concentration
- Others

Identification of Potentially Toxic Species

It should be noted that chlorine, itself, is toxic to most aquatic organisms. For this and other reasons chlorine is perhaps the most widely applied chemical for biofouling control in power plant cooling systems. White (20) reported that current biofouling practices for various cooling circuits in power plants involve two simultaneous types of chlorination: continuous and intermittent. Continuous, low level chlorination (concentration typically 0.25 to 0.50 mg/l (ppm)) is used to control hard shell organisms; and intermittent chlorination (concentration typically 1.0 mg/l (ppm)) is used to control soft form organisms. These chlorine concentrations within the cooling circuit will normally control and/or curtail biofouling problems.

As noted in Section 3.0 (Characterization of Chlorinated Seawater) it is difficult, at best, to predict the products formed by chlorinating natural seawater. This is due to a number of controllable and uncontrollable factors which include: (1) the chemical composition of the seawater (especially ammonia and organic amines); (2) the amount of chlorine added; (3) the reaction duration; and (4) pH and temperature. However as noted, the equilibrium species formed are expected to be predominantly brominated compounds analogous to chlorinated species produced in fresh water.

Preliminary studies conducted by Sugam (8) and Johnson (11) indicated that brominated compound, such as organic and inorganic bromamines, are formed in chlorinated seawater and that these brominated species may have toxic effects. Their work has been substantiated by the preliminary results of Bean et.al. (27) in their analysis of chlorinated seawater discharged from a system similar to a power plant cooling circuit.

A cursory list of the chemical compounds which Bean et.al. (27) identified as being present in chlorinated seawater is given in Table 11. Because this list is preliminary it is expected that the number and types of compound identified will greatly increase as more data become available.

The toxicity of the various chemical species (particularly brominated compounds) which may be formed as a result of seawater chlorination has not been established; however, Bean (27) found that the principal constituents found in chlorinated seawater is bromoform which is one of the compounds identified in the list of 129 priority pollutants. Various other brominated substances listed in Table 11 such as bromo biphenyls are also contained in the same list, and bromonaphthalene which have a chlorinated analog are also contained in this list.

The fact that those compounds identified by Bean et.al. (27) are so closely linked to species that have been previously identified as being toxic is indicative, that the conclusion reached by Sugam and Johnson, of many of the brominated species formed will be toxic may be indeed correct.

TABLE 11. A PRELIMINARY LIST OF THE CHEMICAL CONSTITUENT IDENTIFIED IN CHLORINATED SEAWATER

1. Bromoform	10. Dimethylnaphthalenes
2. Trimethylbenzene	11. Bromonaphthalene
3. Naphthalene	12. Bromomethylnaphthalenes
4. Bromotrimethylbenzene	13. Bromobiphenyls and Bromodimethylnaphthalenes
5. 2-Methylnaphthalene	
6. 1-Methylnaphthalene	14. Phenanthrene
7. Biphenyl	15. Bromotrimethylnaphthalene
8. Bromotetraline	16. Phthalate Esters
9. Bromotetramethylbenzene	17. Pyrene
	18. Bromoacetal

Identification of Toxic Levels and Aquatic Organisms Affected

This sub-section presents information on the toxicity of chlorinated seawater and the marine organisms which may be affected.

In order to conduct a meaningful evaluation of the toxic effects of chlorinated seawater a broad data base is required. This data base must include information identifying the organism being studied, the toxicant and its maintained concentration, as well as the exposure time. The response of several different organisms, including plants, hard-shell animals, and fish, to various concentrations of the toxicant at different exposure times should also be studied.

The following is a compilation of the results of toxicity tests conducted by several different researchers on the effects of chlorinated seawater on various marine organisms:

Mattice and Zittell (28) compiled a rather extensive list which shows the toxicity of chlorine to various marine organisms. A modified version of this list is shown in Table 12. In compiling this information they analyzed data from approximately twenty studies to develop, whenever possible, the 50 percent mortality level and/or mortality threshold. They concluded that at concentrations below 0.02 mg/l (ppm), chlorine had no lethal effects on marine organisms. Consequently a chronic toxicity threshold at 0.02 mg/l (ppm) chlorine and an acute toxicity threshold which is concentration and exposure time dependent were established by these researchers.

Becker and Thatcher (29) compiled toxicity data of various power plant chemicals on marine organisms. In summarizing the data from several studies they included parameter such as the organisms affected, the concentration and type of toxicant, and the type of test conducted. A modified version of their work is given in Table 13.

The data presented in Table 13 correlate well with the findings of Mattice and Zittell, that is, there is no evidence to indicate that the various toxicants studied have any lethal effect on marine organisms for concentrations less than 0.02 mg/l (ppm). The data also show that the toxicity of various chemicals is dependent upon organism tested, chemical concentration, and exposure time.

TABLE 12. SUMMARY OF DATA ON TOXICITY OF CHLORINE TO MARINE ORGANISMS

Data Point and Scientific Name	Descriptive Name	Concentration (mg/l)	Duration (min)	Effect
Plants:				
N.G.	Phytoplankton	0.1	240	71% decrease in productivity
N.G.	Phytoplankton	0.03	N.G.	50% decrease in photosynthesis
Chlorophyta				
Chiamydomonas sp.		1.5	5-10	Decreased grwoth
Dunaisella terliolecia		0.11	1,440	50% decrease in growth
Chrysophyta				
Asterionella Japonica		0.4	0.27	50% decrease in growth
Asterionella japonica		0.2	2	50% decrease in growth
Chaetoceros decipiens		0.14	1,440	50% decrease in growth
Chaetoceros didymum		0.125	1,440	50% decrease in growth
Delonula confervacea		0.8	0.6	50% decrease in growth
Skeletonema costatum		0.095	1,440	50% decrease in growth
Skeletonema costalum		0.6	1.7	50% decrease in growth
Thalassiosira nordenshoikii		0.195	1,440	50% decrease in growth
Thalassiosira Pseudonana		0.075	1.440	50% decrease in growth
Thalassiosira pseudonana		0.2	6.8	50% decrease in growth
Thalassiosira pseudonana		0.5	0.3	50% decrease in growth
Thalassiosira rotula		0.33	1,440	50% decrease in growth
Chrysophyceae				
Monochrysis lutheri		0.2	1,440	50% decrease in growth
Rhodomonas baltica		0.11	1,440	50% decrease in growth

(Continued)

TABLE 12. (Continued)

Phaeophyta				
Macrocystis pyrifera	Giant kelp	5-10	5,760	50% decrease in photosynthesis
Invertebrate animals:				
Cnidaria				
N.G.	Sea anemone	1.0	21,600	No effect
Bimeria franciscana	Hydroid	2.5	180	Slight decrease in growth
Annelida				
Phragmatopoma californica	Polychaete worm	0.2	5	17% decrease in sperm motility
Phragmatopoma californica	polychaete worm	0.4	5	70% decrease in sperm motility
Mollusca				
Crassostrea virginica	Oyster	0.2	N.G.	~46% decrease in ciliary beat rate
Crassostrea virginica	Oyster	1.0	20-90	Pumping threshold
Crassostrea virginica	Oyster	0.18	4,320	50% decrease in time open
Ostrea edulis	Oyster larvae	0.5	2	Swimming stopped
N.G.	Oysters	2.5	10	No effect (30°C)
Mylilus edulis	Mussel	1.0	21,600	100% mortality
Mylilus edulis	Mussel	2.5	7,200	100% mortality
Mytilus edulis	Mussel	0.02-0.05	N.G.	Young won't attach-attached ones will move
Crepidula and Littorina	Gustropods	0.2	N.G.	Stops growth
Acartia tonsa	Copepod	0.75	2	30% mortality @ 20°C after 96 hr
Acartia tonsa	Copepod	0.75	2	70% mortality @ 25°C after 96 hr.
Acartia tonsa	Copepod	1	120	50% mortality
Acartia tonsa	Copepod	10.0	0.7	50% mortality
Acartia tonsa	Copepod	2.5	5	90% mortality-after 3 hr.
Eurylemora affinis	Copepod	1	300	50% mortality
Eurylemora Affinis	Copepod	10.0	2	50% mortality

(Continued)

TABLE 12. (Continued)

Pseudodiaptomus coronatus	Copepod	2.5	45	50% mortality
Pseudodiaptomus coronatus	Copepod	10	5	50% mortality
Balanus improvisus	Barnacle larvae	2.5	5	80% mortality-after 3 hr.
N.G.	Barnacles	1.0	21,600	Most dead
Elminius modestus	Barnacle nauplii	0.5	10	Threshold mortality
Elminius modestus	Barnacle nauplii	1	10	Heavy losses-no growth
Corophium sp.	Tube dwelling amphipod	10	410	No mortality after 24 hr.
Gammarus tigrinus	Amphipod	2.5	180	25% mortality after 96 hr.
Melita nilida	Amphipod	2.5	120	50% mortality
Melita nilida	Amphipod	2.5	5	Some mortality
Callinecles sapidus	Blue crab	10	1,140	50% mortality
Callinecles Sapidus	Blue crab	0.1	5,760	50% mortality
Crangon septemspinosus	Sand shrimp	0.15	900	50% mortality
Crangon septemspinosus	Sand shrimp larvae	5	10	42% mortality
Crangon septemspinosus	Sand shrimp larvae	10	5	55% mortality
Palaemonetes pugio	Grass shrimp	2.5	180	98% mortality-after 96 hr.
Ectoprocta				
Bugula sp.		2.5	2,880	100% mortality
Bugula sp.		10	1,440	100% mortality
Echinodermata				
Strongylocentrotus purpuratus	Sea urchin	0.125	5	1-6% fertilization success
Urechis caupo	Echiuroid	0.2	5	78% fertilization success
Urechis caupo	Echiuroid	0.4	5	0% fertilization success
Chordata				
Botryllus sp.		10	1,440	100% mortality
Molgula sp.		1	4,320	100% mortality

(Continued)

TABLE 12. (Continued)

Vertebrate animals:				
Pleuronectidae				
Limanda ferruginea	Yellowtail flounder	2.5	1,440	50% mortality
Pleuronectes platessa	Plaice larvae	0.028	5,760	50% mortality
Pleuronectes platessa	Plaice larvae	0.05	460	50% mortality
Pleuronectes platessa	Plaice larvae	0.075	75	50% mortality
Pleuronectes platessa	Plaice larvae	0.25	4,320	Mortality threshold
Pseudopleuronectes americanus	Winter flounder	2.5	15	50% mortality
Pseudopleuronectes americanus	Winter flounder	10.0	0.3	50% mortality
Pseudopleuronectes americanus	Winter flounder eggs	10.0	20	No mortality
Salmonidae				
Oncorhynchus gorduscha	Pink salmon	0.05	5,760	50% mortality
Oncorhynchus gorduscha	Pink salmon	0.5	7.5	50% mortality ($13.6^{o}C$)
Oncorhynchus gorduscha	Pink salmon	0.25	15	50% mortality ($13.6^{o}C$)
Oncorhynchus kisutch	Coho salmon	0.08	7,200	50% mortality
Oncorhynchus tshawytscha	Chinook salmon	0.1	60	Distressed-no mortality
Oncorhynchus tshawytscha	Chinook salmon	0.25	130	Mortality threshold
Oncorhynchus tshawytscha	Chinook salmon	1.0	23	Mortality threshold
Oncorhynchus tshawytscha	Chinook salmon	0.5	7.5	50% mortality ($11.7^{o}C$)
Oncorhynchus tshawytscha	Chinook salmon	0.25	30	50% mortality ($11.7^{o}C$)
Oncorhynchus tshawytscha	Young salmon	0.05	33,123	Threshold mortality
N.G.				
Atherinidae				
Menidia menidia	Atlantic silverside	0.58	90	50% mortality
Menidia menidia	Atlantic silverside	1.2	30	50% mortality

(Continued)

TABLE 12. (Continued)

Clupeidae				
Alosa aestivalis	Blueback herring	0.67	60	50% mortality
Alosa aestivalis	Blueback herring	1.2	15	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.22	60	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.7	10	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.21	300	50% mortality
Brevoortia tyrranus	Atlantic menhaden	1.2	30	50% mortality
Brevoortia tyrranus	Atlantic menhaden larvae	0.5	3	0 mortality
Gasterosteidae				
Gasterosteus aculeatus	Threespine stickleback	0.09-0.13	5,760	50% mortality
Ameiuridae				
Ictalurus catus	White catfish	0.1	2,880	50% mortality
Cyprinidae				
Notemigonus chrysoleucas	Golden shiner	0.03-0.23	5,760	50% mortality
Bothidae				
Paralichthys sp.	Flounder	0.3	5	Threshold mortality
Mugilidae				
Mugil cephalus	Striped mullet juveniles	0.3	5	Threshold mortality
Miscellaneous				
N.G.	Marine fish	1.0	1	Slight irritant response

TABLE 12. (Continued)

Clupeidae				
Alosa aestivalis	Blueback herring	0.67	60	50% mortality
Alosa aestivalis	Blueback herring	1.2	15	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.22	60	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.7	10	50% mortality
Brevoortia tyrranus	Atlantic menhaden	0.21	300	50% mortality
Brevoortia tyrranus	Atlantic menhaden	1.2	30	50% mortality
Brevoortia tyrranus	Atlantic menhaden larvae	0.5	3	0 mortality
Gasterosteidae				
Gasterosteus aculeatus	Threespine stickleback	0.09-0.13	5,760	50% mortality
Ameiuridae				
Ictalurus catus	White catfish	0.1	2,880	50% mortality
Cyprinidae				
Notemigonus chrysoleucas	Golden shiner	0.03-0.23	5,760	50% mortality
Bothidae				
Paralichthys sp.	Flounder	0.3	5	Threshold mortality
Mugilidae				
Mugil cephalus	Striped mullet juveniles	0.3	5	Threshold mortality
Miscellaneous				
N.G.	Marine fish	1.0	1	Slight irritant response

TABLE 13. SUMMARY OF THE TOXICITY OF VARIOUS CHEMICAL SPECIES TO MARINE ORGANISMS

Chemical Compound	Test Organism	Test Conditions	Concentration (ppm)	Remarks
Chlorine	Mussels	CB,FS	2.5	Total kill, 5-8 days, constant exposure, all organisms
	Barnacles & sea anemones		1.0	Some barnacles, all anemones alive after 15 days.
			10.0	All tunicates and bryozos killed, 1 hr/day exposure.
	Tunicates & bryozos		10.0	Incomplete kill of adult mussels & anemones, h r/day exposure.
			10.0	Some barnacles survived, 4 hr/day exposure.
Chlorine	Oncorhynchus kisutch	CB,LS	0.08-0.1	"Critical level" for 3-day exposure, all species.
	O. tshawytscha		≈0.05	"Lethal limit," up to 23 days, all species.
	O. gorbuscha		0.05	Maximum nonlethal.
	O. kisutch		0.05	Maximum nonlethal.
Chlorine	Kuhlia sandvicensis	LS	1.0	Slight irritant response. Violent irritant response. (2 min exposure)
			10.0	
Chlorine	Crassostrea virginica (oyster)	CB,LS	0.01-0.02	Sensitive to initial exposure, reduce pumping and close valves; later develop tolerance.
			0.2	Reduce beat frequency of cilia, 21-22 C.
			0.01-3.0	Causes no injury to tissue.
			0.01-0.05	Interfers with normal functioning.

(Continued)

TABLE 13. (Continued)

Chlorine	Elminius modestus (barnacle nauplii)	SB,LS	0.5	10 min exposure, "little effect."
			1.0	"Significant decrease" in survival after 10 min exposure.
	Ostrea edulis (oyster larvae)		2.5-5.0	10 min exposure, "little harm" at temperatures as high as 30°C.
			3.0-6.0	12 & 20 min exposures, "little effect;" ≈ 19 C.
Chlorine	"fish"	---	0.11-0.13	Lethal.
Chlorine	Macrocystis pyrifers (marine Kelp)	CB,LS	1.0	No effect on photosynthesis, 5 days.
			5-10	50% reduction of photosynthesis, 4 days.
Chlorine	"phytoplankton" (estuarine)	LS & FS	---	Concentration not measured; 50-91% reduction of photosynthesis after passing through power plant believed due to chlorine.
Chlorine	Bimeria franciscana (hydroid)	CB,LS	4.5	No effect after 3 hr exposure.
Chlorine	Cnlamydomonas sp. (marine plankton)	SB,LS	1.15	Time-lag in growth, 5-10 min exposure
			20.0	Growth affected, recovered in 9 days.
	Skeletonema costatum (marine plankton)		0.40-0.65	Adverse effect on growth, 5 min exposure.
			2.0	No growth 30 days after treatment.

(Continued)

TABLE 13. (Continued)

Chlorine	"marine organisms"	FS	0.5	Continuous chlorination controls marine organisms; 5-6 ppm used during shut-down. (Methods applied are described)
Sodium hypochlorite (chlorox)	Kuhlia sandvicensis	LS	10.0	Violent reactive response.
			2.0	Violent reactive response (2 min exposure).
Sodium pentachlorophenate	Kuhlia sandvicensis	LS	20.0	Medium reaction, 2 min exposure
Sodium pentachloro phenate	Crassostrea gigas (oyster)	LS	0.027	4.3% abnormal embryos in 48 hr.
			0.069	72.4% abnormal embryos in 48 hr.
			0.11	100% abnormal embryos in 48 hr.
Sodium pentachlorophenate	Mylilus edulis (bay mussel)	LS	0.20	12% abnormal embryos, 28 ppt salinity
			0.20	21% abnormal embryos, 24 ppt salinity
			0.30	17.6% abnormal embryos, 28 ppt salinity
			0.30	33.6% abnormal embryos, 24 ppt salinity
			0.4	22.1% abnormal embryos, 28 ppt salinity
			0.4	69.1% abnormal embryos, 24 ppt salinity

(Continued)

TABLE 13. (Continued)

Pentachlorophenol	Macrocystis pyritera (kelp)	LS	2.66	Eliminated all photosynehesis in 4 days.
			1.0	Eliminated photosynthesis in 2 days.
Sodium pentachloro-phenate (Sanobrite)	Macrocystis pyritera (kelp)	CB,LS	0.3	50% inactivation of photosynthesis in 4 days
Sodium pentachloro-phenate (Santobrite)	"mussel, anemones, barnacles"	SB,LS	0.1	Ineffective.
			1.0	Killed all organisms, 3 days.
		CB,LS	10.0	Killed all anemones, tunicates, and bryozos in 1 day; all barnacles in 3 days, all mussels in 5 days.
			1.0	Killed all tunicates and bryozoa in 1 day; all anemones, mussels and barnacles in 4 days.
Bromine	Kuhlia sandvicensis	LS	1.0	No irritant response, (2 min exposure)
			10.0	Violent irritant response.

LEGEND:

SB = Static bioassay
CB = Constant-flow bioassay
LS = Lab study
FS = Field study

In his discussion of the toxicity of chlorine on aquatic life, Brung (30) cited a laboratory study with synthetic seawater. This study demonstrated that phytoplankton (Cyclofella nana), when exposed to residual chlorine concentrations of 0.150 mg/l for more than 10 to 20 minutes, showed inhibited growth patterns. With residual concentrations of chlorine greater than 0.45 mg/l for 6 seconds exposure time, similar growth inhibition patterns occured.

In recent studies conducted by Goldman et.al. (31) it was found that the metabolic activity of larval zooplankton was seriously affected at chlorine residual levels below the level of detectability (< 0.01 mg/l). This was found as a result of exposing the larvas to chloramine in concentrations < 0.01 mg/l for 30 minutes under controlled conditions.

Another recent study by Erickson and Freeman (32) evaluated the effect of various chlorinated and brominated compounds on four species of marine phytoplankton. They studied the toxic effect of chloroform and bromoform on the phytoplankton and found no noticeable impact occurred at concentration of 32 mg/l for either compound. However they discovered that monochloramine inhibits cell division at concentration as low as 0.125 mg/l utilizing seawater under laboratory controlled conditions.

Given the above information and data presented in the earlier portion of this document, it is expected that various organo-bromides analogous to the organo-chlorides discussed in Section 3.0 (Characterization of Chlorinated Seawater) will be formed. The toxicity of these brominated species on aquatic organisms have not been clearly established. However, since toxicity is a function of concentration and time, and since bromamines are more labile as a group than chloramines and are more readily reduced to their constituents (Johnson (11)),one could make the supposition that brominated species may not be as toxic as the chlorinated analogs. Assuming that both species are present in equivalent concentrations, and that both have comparable toxicities, the brominated species will decay more quickly and consequently its toxic effect will be dissipated more rapidly.

Actual toxicity information on the various species formed in chlorinated seawater is scarce. Currently, Battelle Pacific Northwest and the University of Maryland are conducting independent studies to evaluate the

toxicity of compounds formed by chlorinating seawater. The Battelle study involves the comparative assessment of toxicity between chloroform and bromoform on aquatic organisms. Four marine water organisms (Quahaug, East Coast Oyster, White Shrimp and Atlantic Menhaden), are being evaluated for bromoform toxicity. Concurrently four freshwater species of fish (Blue Gill, Small Mouth Bass, Channel Catfish and Rainbow Trout) are studied for their reactions towards chloroform. Both of these are in-situ,continuous flow through studies. Although preliminary data have been compiled, actual findings or conclusions are not currently available for inclusion in this report. The University of Maryland was conducting similar biological studies except their effort was directed preimarily at evaluating the "net toxic effects" of chlorinated seawaters from power plants. The completed report of their studies have not been published at this time. Preliminary communications with the author revealed that: (1) bromoform may not be the most toxic constituent from seawater chlorination because of its high volatility; further studies are needed to characterize other brominated species; (2) Blue Crabs are most tolerant to chlorination or products of chlorination; (3) oysters and their larvae, being the most sensitive species to chlorination, are more susceptible to chlorine toxicity at lower than at higher concentrations. This is due primarily to oysters' inability to detect low chlorine dosages and their ability to biosynthesize anaerobically under stress or at high chlorine dosages.

Comparison of Toxic Levels with Levels Expected from Power Plant Discharges

In his discussion of continuous chlorination as applied to power plant cooling circuits, White (20) stated that, to achieve adequate biofouling protection, the concentration levels of free chlorine residual at the condenser tailpipes should be maintained at 0.25 to 0.50 mg/l (ppm). As previously noted, at these levels, chlorine has toxic effects on certain marine organisms. These levels are within the cooling circuit, and the typical power plant cooling circuit is designed to retain the cooling water from 5 to 10 minutes. Because of chlorine demand and/or decay, the majority of the free chlorine residual will combine with other seawater components and form new chlorinated organic species.

In papers presented by Sugam (8) and Johnson (11), the decay of chlorine by oxidation-reduction reactions with various halides and amino-nitrogen compounds present in seawater was discussed. Both concluded that chlorine is short-lived in seawater and that the major components in chlorinated seawater would be oxidants of chlorine and bromine as well as organic and inorganic halogenated amines. Thus, the "free chlorine residual" would be converted to "combined residual chlorines". Other studies conducted by Carpenter et. al. (9) and Hostgaard-Jensen et.al. (33) resulted in similar findings. Carpenter's work supported much of Johnson's findings regarding the presence of a large amount of brominated species in chlorinated seawaters.

Hostgaard-Jensen et.al. (33) also concluded that chlorine decay could occur as a result of reactions with organic material and other chemical species present in seawater; thus, the chlorine could be reduced to organic ionic and/or chlorides. They then studied the decay of chlorine residuals in cooling water upon discharge into water bodies. In these studies they found that laboratory experiments predicted chlorine residual concentrations approximately twice as high as those actually measured in field tests. In field tests they found that the discharge water contained 1.0 mg/l residual chlorine and within 100 meters of the outfall the residual chlorine concentration was between 0.05 to 0.10 mg/l.

In his study of five California power plants Hergott et al. (12) found that if a free chlorine residual concentration of 0.50 mg/l (ppm) was maintained at the condenser tailpipes, the maximum total oxidant residual at the outfall would be 0.16 mg Cl_2/l which would decrease to approximately 0.09 mg Cl_2/l within 50 feet (15.3 m).

The reduction in chlorine concentration from the cooling water outfall to some distance away from the outfall is due to two factors: chlorine decay by chemical reactions and effluent dilution. Both of these factors are of importance in analyzing the toxicity of chlorinated cooling water effluent.

By comparing the chlorine residual concentrations in the outfall of the power plant cooling systems discussed above with the toxicity information present in the Toxic Level Section, it can be seen that the chlorine levels in

cooling water discharges can be toxic to certain marine organisms. The degree of toxicity is, however, dependent upon the organism exposed and the exposure time. The reaction of soft organisms, slime and sponges, to chlorine is in some respects quite different than that of hard-shelled organisms, such as mussels and barnacles. Some organisms, which are identified in Tables 12 and 13, show great tolerances to high levels of chlorine for short exposure times while they are quite intolerant to low level concentrations for long exposure times. Other organisms adapt readily to low level concentrations and long exposure times but respond violently to high levels for short exposure time. It is for this reason that biofouling control techniques incorporate continuous low level chlorination in conjunction with intermittent high level chlorination.

Qualitative Analysis of the Toxicity and Measurement of Pollutants Formed in Chlorinated Seawater

This section will discuss the information previously presented and points out areas where data gaps exist. A discussion of the amperometric titration method and how well it can be used to measure oxidants from chlorination is also included.

As pointed out by Johnson (11) the major problem that confronts the research in determining the toxicity of compounds found in chlorinated seawater is the identification of chemical species that are actually present. According to Johnson the major species of concern are: bromine, chloramines, and bromamines; each of these components have a high probability of causing toxic effects to marine life. Sugam (8) in his discussion of the various species of chlorine produced oxidants supported Johnson's position. They both concluded that chlorine was short-lived in seawater, and that in the absence of amino-nitrogens in seawater (pH8) the majority of the species measured as "residual chlorine" would be bromine. When amino-nitrogen is present the formation of organic and inorganic halo-amines competes with the formation of bromine. The formation of halo-amines is favored kinetically by high pH, low salinity, high amino-nitrogen levels and high amino-nitrogen to chlorine ratios. Carpenter et.al. (9) in their study of halogen chemistry concluded, as did Sugam and Johnson, that chlorine reacts with bromide to form bromine

species and chloride ions. They further concluded that the halo-organics formed by chlorinating seawater are likely to be brominated species.

Currently, studies by the University of Washington, the University of North Carolina, and Battelle Pacific Northwest are being conducted to identigy the various species formed by the chlorination of seawater. Preliminary findings indicate that the chemistry involved is quite complex and that the species formed are highly dependent upon the characteristics of the intake water (including water quality and salinity, season of the year, and residence time in the cooling circuit).

The results of these studies and toxicity testing of the various species formed will be necessary in order to formulate any meaningful data on the toxic effects to marine life. If, however, assuming that the information supplied by Sugam, Johnson, and Carpenter is indicative of the chemical species found in chlorinated seawater and comparing this information with current testing techniques, a number of interesting anomalies occur. Sugam (25), in more recent studies, found that these brominated species plus others cause interferences in amperometric titration readings, and that bromamines cannot be clearly separated from free chlorine or bromine. Because the amperometric method measures bromine and iodine residuals in addition to chlorine residuals, Hergott et al, (1) referred to the results of amperometric titration tests conducted on chlorinated seawater as "oxidant residuals" rather than "chlorine residuals".

The amperometric titration testing method was discussed in detail in Section 4.0. It is found that the amperometric titration method appears to be adequate in any determinations involving toxic oxidants that may be produced by the chlorination of seawater. Although the measurement of individual species from chlorination may not be possible, a relatively accurate determination of the total oxidants can be made. As suggested by Johnson (11) and discussed by Goldman et al. (31) and Ericson et al. (32), compounds such as bromamines, chloramines and various other brominated species which cause interferences to the method may have toxicities equal to or greater than the chlorine itself. If these compounds are perceived as total oxidant residual rather than free chlorine residual, then the amperometric titration method may be applicable.

If it becomes necessary to monitor individual components in the cooling water discharge stream, then more advanced analytical methods will have to be developed. Concurrent with analytical method development, studies of the toxicity of individual as well as combined components must be undertaken.

Mattice and Zittel (28) developed a graph to show the toxicity of "residual chlorine" to marine organisms. The graph summarzied data from various other research studies. Figure 7 presents a slightly modified version of that graph. This graph contains estimates of both acute and chronic toxicity thresholds. The implication of the graph is that if a dose-time combination is lower than the chronic toxicity threshold or to the left of the acute toxicity threshold no mortality is likely to occur as a result of chlorination. Mattice and Zittel developed the "threshold line" using data which were, for the most part, 50 percent effect levels on either mortality or sublethal physiological rates, and then adjusting the line to zero mortality levels. As shown on the graph, concentrations below 0.02 mg/l have no lethal effect regardless of an increase in exposure time.

Comparing "free residual chlorine" levels developed by current practices in power plant cooling circuits with the toxicity threshold shown in Figure 7 it can be seen that the target levels (0.25 - 1.0 mg/l) developed within the cooling circuit will produce "acute toxic effects" on marine life for exposure times greater than 2 1/2 minutes (at lower concentration limits), and less than one minute (at the upper concentration limit).

As has already been discussed,if rather than measuring "chlorine residual" the amperometric titration method measure "oxidant residual" and if the effluent stream is shown to be toxic then current standards should be revised to place a limit on the "oxidant residual" rather than "chlorine residual" in the effluent stream.

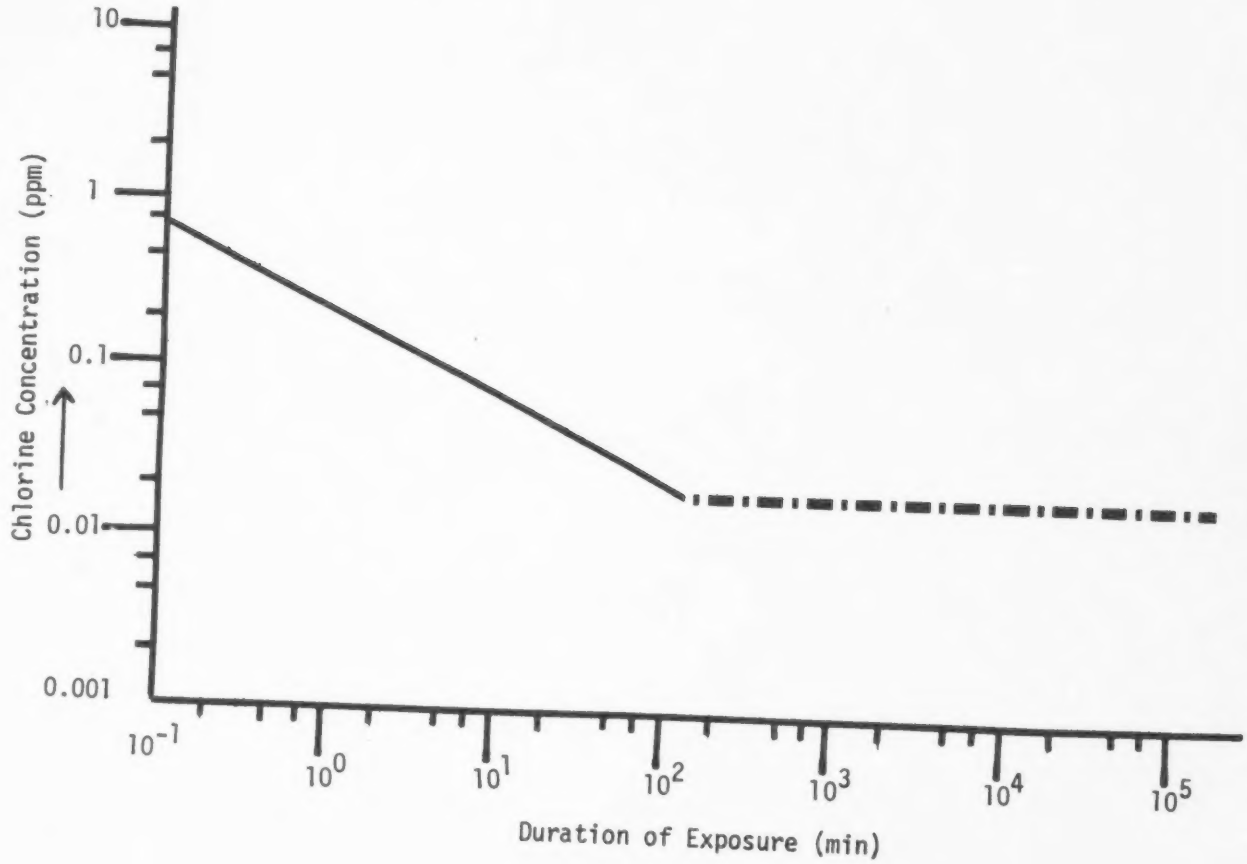


Figure 7. Toxicity of chlorine to marine organisms (22)

REFERENCES

1. Hergott, S., et.al., Power Plant Cooling Water Chlorination in Northern California, University of California, Berkeley, UCB/SERL No. 77-3, August 1977.
2. Yu, H.H.S., et.al., Alternatives to Chlorination for Control of Condenser Tube Bio-Fouling, Monsanto Research Corp., EPA-600/7-77-030, March 1977.
3. Federal Register, Vol. 39, No. 196, Oct. 8, 1974.
4. Todd, D.K., editor, The Water Encyclopedia, Water Information Center, 1970.
5. Smith, F.G.W., editor, Handbook of Marine Science, Vol. 1, CRC Press, 1974.
6. Strickland & Parsons, A Practical Handbook of Sea Water Analysis, Fisheries Research Board of Canada, Bulletin No. 167, 2nd. ed., 1972.
7. Liptak, B.G., editor, Environmental Engineers Handbook, Vol. 1, Water Pollution, Chilton Book Company, 1974.
8. Sugam, R. and G.R. Helz, Speciation of Chlorine Produced Oxidants in Marine Waters: Theoretical Aspects. Chesapeake Science, Vol. 18, No. 1, page 113-116.
9. Carpenter, J.H. and D.L. Macalay, Chemistry of Halogens in Seawater. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.
10. Johnson, J.D., Measurement and Persistance of Chlorine Residuals in Natural Water. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.
11. Johnson, J.D., Analytical Problems in Chlorination of Saline Water. Chesapeake Science, Vol. 18, No. 1, page 116-118.
12. Davis, W.P. and D.P. Middaugh, A Review of the Impact of Chlorination Processes Upon Marine Ecosystems. Proceedings of the Conference on The Environmental Impact of Water Chlorination. Oak Ridge, Tennessee, October 22-24, 1975.
13. Jolley, R.J., G. Jones, W.W. PiH, and J.E. Thompson, Chlorination of Organics in Cooling Waters and Process Effluents. Proceedings of the Conference on The Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.
14. Carpenter, J.H., and C.A. Smith, "Reactions in Chlorinated Seawater", Water Chlorination Environmental Impact and Health Effects; Vol. 2, editor R.J. Jolley et.al., Ann Arbor Science, 1978.
15. Kovacic, P., M.K. Lowery, and K.W. Field, Chemistry of N-Bromamines and N-Chloramines. Chemical Reviews, 1970, Vol. 70, No. 6, pp. 639-665.

16. Marks, H.C. and Glass, J.R., "A New Method of Determining Residual Chlorine", JAWWA Vol. 34, 1942, pp. 1227-1290.

17. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 322-325, 1975.

18. American Society for Testing and Materials, 1977 Annual Book of ASTM Standards, pp. 292-298, 1976.

19. Carpenter, James A., et.al., "Errors in Determination of Residual Oxidants in Chlorinated Sea Water", Environ. Sch. and Tech., 11(10) pp. 992-994, Oct. 1972.

20 White, G.C., Handbook of Chlorination, Van Nostrand Reinhold Co., N.Y. 1972, pp. 264.

21. Bradbury, J.H. and A.N. Hambly, "An Investigation of Errors in the Amperometric and Starch Indicator Methods for the Titration of Millinormal Solutions of Iodine and Thiosulfate" Australian J. Sci. Res., Ser. A, 5 pp. 541-554.

22. Wong, G.T.F. and P.G. Brewer, "The Marine Chemistry of Iodine in Anoxic Basins", Geochim. Cosmochim Acta, 41, pp. 151-159 (1971).

23 Abel, E. and F. Fabian, "Kinetics of the Halogenate-Halide Reaction in Heavy Water", Monatsch. 71, pp. 153-175 (1938).

24. Cizecelius, E.A., et.al., "Errors in Determination of Residual Oxidants in Chlorinated Seawater", Battelle Northwest Labs.

25. Sugam, R., The Chemistry of Chlorine in Estuarine Waters, Unpub. thesis, University of Maryland, College Park, pp. 702 (1977).

26. Burton, D.T., General Test Conditions and Procedures for Chlorine Toxicity Tests with Estuarine and Marine Macroinvertebrates and Fish. Chesapeake Science Vol. 18, No. 1, pp. 130-136, March 1977.

27. Bean, R.M., R.G. Riley and P.W. Ryan, Investigation of Halogenated Components Formed from Chlorination of Marine Water, Water Chlorination Environmental Impact and Health Effects, Vol. 2, editor R. L. Jolley et.al., Ann Arbor Science, 1978.

28. Mattice, J.S., and H.E. Zittel, Site-Specific Evaluation of Power Plant Chlorination. Journal of Water Pollution Control Federation, Vol. 48, No. 10, pp. 2284-2308, October 1976.

29. Becker, C.D. and T.O. Thatcher, Toxicity of Power Plant Chemicals to Aquatic Life. Battelle Pacific N.W. Laboratories, U.S. Atomic Energy Commission, WASH-1249, June 1978.

30. Brung, W.A., Effects of Residual Chlorine on Aquatic Life. Journal of the Water Pollution Control Federation, Vol. 45, No. 10, pp. 2180-2193, October 1973.

31. Goldman, J.C., J.M. Coppuzzo and G.T.F. Wong, "Biological and Chemical Effects of Chlorination at Coastal Power Plants, Water Chlorination Environmental Impact and Health Effects, Vol. 2, editor R.L. Jolley et.al., Ann Arbor Science, 1978.

BIBLIOGRAPHY

Abel, E. and F. Fabian, "Kinetics of the Halogenate-Halide Reaction in Heavy Water", Monatsch. 71, pp. 153-175 (1938).

American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 322-325, 1975.

American Society for Testing and Materials, 1977 Annual Book of ASTM Standards, pp. 292-298, 1976.

Baker, R.J., Types and Significance of Chlorine Residuals. Journal of AWWA. 51 (9), September 1959.

Basch, R.E., and J.G. Truchan, Toxicity of Chlorinated Power Plant Condenser Cooling Water for Fish. EPA Report No. 600/3-76-009, April 1976.

Bean, R.M., R.G. Riley and P.W. Ryan, Investigation of Halogenated Components Formed from Chlorination of Marine Water, Water Chlorination Environmental Impact and Health Effects, Vol. 2, editor R. L. Jolley et al., Ann Arbor Science, 1978.

Becker, C.D. and T.O. Thatcher, Toxicity of Power Plant Chemicals to Aquatic Life. Ba-telle Pacific N.W. Laboratories, U.S. Atomic Energy Commission, WASH-1249, June 1978.

Bellanca, M.A. and D.S. Baily, Effects of Chlorinated Effluent on the Aquatic Ecosystem in the Lower James River, JWPCF, April 1977.

Bender, M.E., et al, Effects of Residual Chlorine on Estuarine Organisms. Biofouling Control Proceedings Technology and Ecological Effects. Marcel Dekker, Inc. 1977.

Bongers, L.H. and T.P. O'Connor, Bromine Chloride - an Alternative to Chlorine for Fouling Control in Condenser Cooling Systems. EPA Report No. 600/7-77-053, May 1977.

Bongers, L.H., et al., Biotoxicity of Bromide Chloride- and Chlorine-Treated Power Plant Condenser Cooling Water Effluent. Martin Marietta Environmental Technology Center, May 1977.

Bradbury, J.H. and A.N. Hambly, "An Investigation of Errors in the Amperometric and Starch Indicator Methods for the Titration of Milli-normal Solutions of Iodine and Thiosulfate" Australian J. Sci. Res., Ser. A, 5 pp. 541-554.

Brook, A.J. and A.L. Baker, Chlorination at Power Plants. Impact on Phytoplankton Productivity. Science, 72, 176 (4042) pp. 1414-15.

Brung, W.A., Effects of Residual Chlorine on Aquatic Life. Journal of the Water Pollution Control Federation, Vol. 45, No. 10, pp. 2180-2193, October 1973.

Burton, D.T., General Test Conditions and Procedures for Chlorine Toxicity Tests with Estuarine and Marine Macroinvertebrates and Fish. Chesapeake Science Vol. 18, No. 1, pp. 130-136, March 1977.

Cairns, J., et al., Temperature Influence on Chemical Toxicity to Aquatic Organisms. JWPCF, February 1975.

Carpenter, James A., et al., "Errors in Determination of Residual Oxidants in Chlorinated Sea Water", Environ. Sch. and Tech., 11(10), pp. 992-994, October 1972.

Carpenter, J.H., and C.A. Smith, "Reactions in Chlorinated Seawater", Water Chlorination Environmental Impact and Health Effects; Vol. 2, editor R.J. Jolley, et al., Ann Arbor Science, 1978.

Carpenter, J.H. and D.L. Macalay, Chemistry of Halogens in Seawater. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Cizecelius, E.A., et al., "Errors in Determination of Residual Oxidants in Chlorinated Seawater", Battelle Northwest Labs.

Cole, S.A., Chlorination for the Control of Biofouling in Thermal Power Plant Cooling Systems. Biofouling Control Proceedings Technology and Ecological Effects. Marcel Dekker, Inc., 1977.

Davies, R.M. and L.D. Jensen, Zooplankton Entrainment at Three Mid-Atlantic Power Plants. JWPCF, August 1975.

Davis, W.P. and D.P. Middaugh, A Review of the Impact of Chlorination Processes Upon Marine Ecosystems. Proceedings of the Conference on The Environmental Impact of Water Chlorination. Oak Ridge, Tennessee, October 22-24, 1975.

Draley, J.E., The Treatment of Cooling Waters With Chlorine. Argonne National Laboratory, February 1972.

Erickson, S.J. and A.J. Freeman, "Toxicity Screening of Fifteen Chlorinated and Brominated Compounds Using Four Species of Marine Phytoplankton, Ibid.

Fava, J.A. and D.L. Thomas, Use of Chlorine for Antifouling on Ocean Thermal Energy Conversion Power Plants. Gilbert Associates, Inc., 16 June 1977.

Federal Register, Vol. 39, No. 196, October 8, 1974.

Goldman, J.C., J.M. Coppuzzo and G.T.F. Wong, "Biological and Chemical Effects of Chlorination at Coastal Power Plants, Water Chlorination Environmental Impact and Health Effects, Vol. 2, editor R.L. Jolley et al., Ann Arbor Science, 1978.

Haderlie, E.C., The Nature of Primary Organic Films in The Marine Environment and Their Significance for OTEC Heat Exchange Surfaces. Naval Postgraduate School, Monterey, CA. May 1977.

Hamilton, D.H., et al., Power Plants: Effects of Chlorination on Estuarine Primary Production. Science, Vol. 169, 10 July 1970.

Hamilton, D.H., Jr., Chlorination Application for the Control of Condenser Fouling. Water Chlorination, Vol. 2, 1978.

Helz, G.R., et al., Bromoform Production by Oxidative Biocides in Marine Water. Ozone-Chlorine Dioxide Oxidation Products of Organic Material edited by Rice, R.C., et al., 1977.

Hergott, S., et al., Power Plant Cooling Water Chlorination in Northern California, University of California, Berkeley, UCB/SERL No. 77-3, August 1977.

Hirayama, K. and R. Hirano, Influences of High Temperature and Residual Chlorine on Marine Phytoplankton. Marine Biology, Vol. 7, 1970.

Hostgaard-Jensen, P., J. Klitgaard, K.M. Pedersen. Chlorine Decay in Cooling Water and Discharge into Seawater. Journal of the Water Pollution Control Federation, pp. 1832-1841, August 1977.

Johnson, J.D., Analytical Problems in Chlorination of Saline Water. Chesapeake Science, Vol. 18, No. 1, pp. 116-118.

Johnson, J.D. and G.W. Inman, The Effect of Ammonia Concentration on the Chemistry of Chlorinated Sea Water. Water Chlorination, Vol. 2, 1978.

Johnson, J.D., Measurement and Persistance of Chlorine Residuals in Natural Water. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Jolley, R.J., G. Jones, W.W. PiH, and J.E. Thompson, Chlorination of Organics in Cooling Waters and Process Effluents. Proceedings of the Conference on the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Katz, B.M. and U.M. Harder, Attraction of Fish to Chlorine. JWPCF, March 1976.

Katz, B.M., Chlorine Dissipation and Toxicity Presence of Nitrogenous Compounds. JWPCF, July 1977.

Kovacic, P., M.K. Lowery, and K.W. Field, Chemistry of N-Bromamines and N-Chloramines. Chemical Reviews, 1970, Vol. 70, No. 6, pp. 639-665.

Liezke, M.H., A Kinetic Model for Predicting the Composition of Chlorinated Water Discharged from Power Plant Cooling Systems. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Liptak, B.G., editor, Environmental Engineers Handbook, Vol. 1, Water Pollution, Chilton Book Company, 1974.

Marine Research, Inc., A Report on Possible Alternatives to Chlorination for Controlling Fouling in Power Station Cooling Water Systems, 15 April 1976.

Marks, H.C. and Glass, J.R., "A New Method of Determining Residual Chlorine", JAWWA Vol. 34, 1942, pp. 1227-1290.

Mattice, J.C., Assessing Toxic Effects of Chlorinated Effluents on Aquatic Organisms: A Predictive Tool. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Mattice, J.S., and H.E. Zittel, Site-Specific Evaluation of Power Plant Chlorination. Journal of Water Pollution Control Federation, Vo. 48, No. 10, pp. 2284-2308, October 1976.

Morris, J.C., The Chemistry of Aqueous Chlorine in Relation to Water Chlorination. Proceedings of the Conference in the Environmental Impact of Water Chlorination, Oak Ridge, Tennessee, October 22-24, 1975.

Noack, M.G., R.L. Doerr, Reactions of Chlorine, Chlorine Dioxide and Mixtures Thereof with Humic Acid: An Interim Report. Water Chlorination, Vol. 2, 1978.

Perrigo, L.D. and G.A. Jensen, Ocean Thermal Energy Conversion System Biofouling and Corrosion Problems. Battelle Pacific N.W. Laboratories, September 1976.

Roberts, M.H., Jr., Effects of Chlorinated Seawater on Decayed Crustaceans. Water Chlorination, Vol. 2, 1978.

Scott, G.I. and D.P. Middaugh, Seasonal Chronic Toxicity of Chlorination to the American Oyster. Water Chlorination, Vol. 2, 1978.

Skarheim, H.P., Tables of the Fraction of Ammonia in the Undissociated Form for pH 6 to 9, Temperature 0-30°C, TDS 0-300 mg/l, and Salinity 5-35 g/Kg, University of California, Berkeley, SERL Report No. 73-5, June 1973.

Smith, F.G.W., editor, Handbook of Marine Science, Vol. 1, CRC Press, 1974.

Strickland & Parsons, A Practical Handbook of Sea Water Analysis, Fisheries Research Board of Canada, Bulletin No. 167, 2nd. ed., 1972.

Stumm, W., J.J. Morgan, Aquatic Chemistry, An introduction Emphasizing Chemical Equilibria in Natural Water. Wiley-Interscience, 1970.

Sugam, R. and G.R. Helz, Speciation of Chlorine Produced Oxidants in Marine Waters: Theoretical Aspects. Chesapeake Science, Vol. 18, No. 1, pp. 113-116.

Sugam, R., The Chemistry of Chlorine in Estuarine Waters, Unpub. thesis, University of Maryland, College Park, pp. 702 (1977).

Todd, D.K., editor, The Water Encyclopedia, Water Information Center, 1970.

White, G.C., Handbook of Chlorination, Van Nostrand Reinhold Co., N.Y. 1972, pp. 264.

Whitehouse, J.W., Continuous Low-Level Chlorination for Marine Fouling Control at Power Stations in the United Kingdom. Water Chlorination, Vol. 2, 1978.

Wong, G.T.F. and P.G. Brewer, "The Marine Chemistry of Iodine in Anoxic Basins", Geochim. Cosmochim Acta, 41, pp. 151-159 (1971).

Yu, H.H.S., et al., Alternatives to Chlorination for Control of Condenser Tube Bio-Fouling, Monsanto Research Corp., EPA-600/7-77-030, March 1977.